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THE BRITISH JOURNAL OF METALS

Vol 57 No. 343

MAY, 1958

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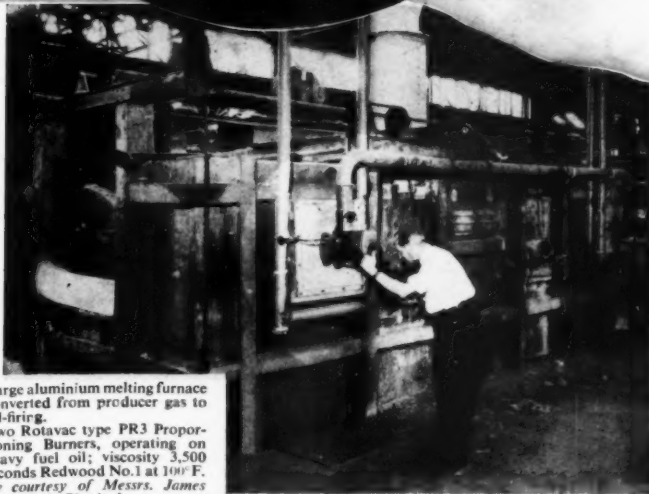
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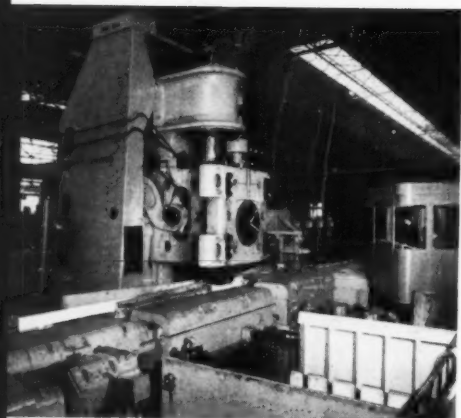
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# METALLURGIA

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INCORPORATING THE METALLURGICAL ENGINEER

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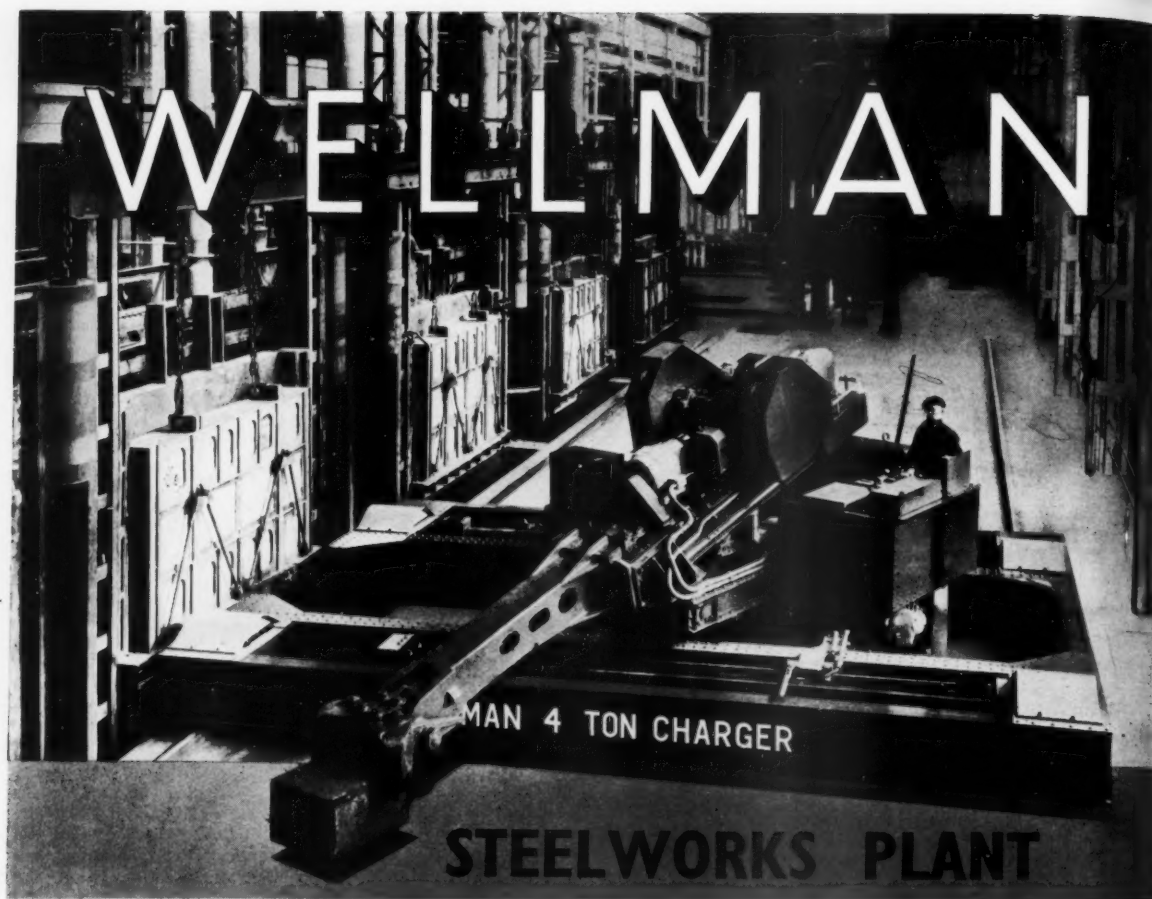
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# METALLURGIA

THE BRITISH JOURNAL OF METALS

INCORPORATING THE "METALLURGICAL ENGINEER"

MAY, 1958

Vol. LVII. No. 343

## Fifty Years of Service

THIS year marks the Golden Jubilee of the Institute of Metals—fifty years of service to the non-ferrous metals industry—and we join with a host of well-wishers in offering our heartiest congratulations on a difficult task well done. Not that it *is* done—in the sense of being finished—for it is calling for greater efforts today than at any time in the Institute's history. Scientific frontiers are advancing so rapidly that the interchange of information and ideas and the publication of scientific and technical papers are more than ever necessary. This is particularly true in the metallurgical field, for whether it be in the realms of nuclear power, space travel, automation, or common or garden engineering, the extent to which progress can be made is likely to be governed by the available materials of construction and the speed with which improvements can be made in them, as was the case with the jet engine, where the development of materials with improved high temperature properties led to greatly improved efficiency in the engine.

At the risk of being accused of parochialism, we, as the only metallurgical journal published in Manchester, take pride in the part which the city has played in the founding of two of our leading metallurgical institutes—the Institute of British Foundrymen, which still has its headquarters here, and the Institute of Metals. The founding of the latter in 1908 was due, as is generally the case, to the enthusiasm of a few individuals. According to the Golden Jubilee Lecture, delivered at the Institute's Annual Spring Meeting on April 28th by Professor R. S. Hulton, Founder Member, the matter was first raised by Mr. W. H. A. Robertson, of Bedford, who, in a letter to *The Engineer* of January 18th, 1908, advocated "the founding of an 'Institution of Copper and Brass Manufacturers.' About a month later, Mr. W. H. Johnson, the first Honorary Secretary, called a meeting in Manchester at which it was resolved 'that a Copper and Brass Institute on similar lines to the Iron and Steel Institute be formed.' The local industry was strongly represented, and H. C. H. Carpenter, who two years before had come to Manchester from the National Physical Laboratory to occupy the new Chair of Metallurgy at the University, was also active. A month later a larger meeting assembled in Manchester, with an assured support of fifty members. An 'Inaugural Meeting' was held in London on June 16th, 1908, at the Institution of Mechanical Engineers. On September 15th, 1908, Gilbert Shaw Scott, aged 24, was appointed Secretary, and on November 12th, 1908, the first General Meeting was held in the Municipal Technical School, Birmingham, presided over by Sir William White, whose Address clearly defined the objects of the Institute. Offices were opened in London early in 1909."

So much for the origins of the Institute: what of the times in which it commenced operations? It will have been noted that the Manchester resolution called for the

forming of an 'Institute of Copper and Brass.' Fortunately, a title indicative of a wider scope was finally adopted, so that not only could the rapid expansion of the aluminium industry be accommodated smoothly and without embarrassment, but the properties and applications of a wide range of non-ferrous metals and alloys could be discussed at the Institute's meetings. Nevertheless, anyone suggesting at the first meeting that the mechanical properties of uranium alloys might one day be a proper subject for discussion would probably have been regarded somewhat curiously. Yet, today, it has been estimated that world production of uranium is of the same order as that of aluminium and nickel in 1908. Several other "newer" metals equal or exceed these figures, and metals which were then almost confined to museum specimens are rapidly becoming available in commercial quantities.

Some realisation of the changes which have taken place during the lifetime of the Institute may be gained from the fact that the first Derby Rolls-Royce car dates from 1908, and the first all-metal aeroplane from 1920. Stainless steel, the essential constituent of which is a non-ferrous metal, was discovered by Harry Brearley in 1912, ductile tungsten for electric lamps by W. D. Coolidge in 1909, and chromium plating by G. J. Sargent in 1920, whilst Duralumin—the first strong aluminium alloy—was produced by Alfred Wilm in 1909.

When the Institute was formed in 1908, the Iron and Steel Institute and the Institution of Mining and Metallurgy were in existence, but the latter was mainly concerned with extraction metallurgy, and only occasionally were matters of common interest to non-ferrous metallurgy published by the Iron and Steel Institute. Occasional articles in the *Journal of the Royal Society of Arts* covered the Institute's field, and on the technical side there were such journals as *Metal Industry* (New York), the *Brass World and Plater's Guide*, and the *Electrochemical and Metallurgical Industry* (all American). The results of research in physical metallurgy were first communicated to the chemical and engineering societies, but soon after the turn of the century other journals came into existence, including the *Metallographist* and the *Revue de Métallurgie*: the *Zeitschrift für anorganische Chemie* (1892) was also of considerable importance. In 1903 the Faraday Society was founded to promote the study of electrometallurgy, metallography, and kindred subjects, and received support from those interested in this field.

One possible yardstick by which to measure the changes which have taken place in the last fifty years is to be found in the demand for technical and scientific staff, as measured by advertisements in the press. Professor Hulton said that in *Nature* in October, 1908, he found only a single advertisement of this type. It sought a "Research Chemist," but specified that he must have £3,000 available for investment! In one issue of the same journal in January, 1958, there were eight pages devoted to vacant appointments.

Having considered the origins and early environment of the Institute, reference may now be made to its activities during its first fifty years. Since its inception the Institute has set a high standard in its acceptance of papers for presentation, and as a result its *Journal* has justly acquired a first-class reputation throughout the world. There is from time to time criticism of the type of paper published, this usually stemming from the 'practical man' who sees, or pretends to see, no value in the 'academic' type of paper. This is a somewhat short-sighted view, for although a balance between theoretical and practical papers is desirable, it is essential that the former be published. On the face of it, it often appears that the results of an investigation of the system A-B (where A and B are two rather obscure metals) are of no interest to anyone but the authors. This may indeed be true, but it is not necessarily a reason for non-publication, for in a few years time the system may have acquired an importance scarcely dreamt of at present, and the industrial metallurgist will then be extremely grateful that he can find some basic information concerning it.

Amongst the original objects of the Institute was the issue of abstracts of papers published elsewhere. Securing a full review of information from world-wide sources is a matter of some difficulty, and there is no doubt that the United Kingdom used to be far behind Germany in this respect. Today, thanks to the efforts of the Institute's Publication Committee, this is no longer true, and the issue of *Metallurgical Abstracts* as a separate volume has placed the Institute in a leading position. The number of abstracts has increased steadily from 190 in the first full year to over 5,500 in 1956/7. Many of the periodicals abstracted are available to members, together with books covering the scientific and industrial sides of metallurgy, through the Library, which is administered jointly with the Iron and Steel Institute.

The primary purpose of the General Meetings of the Institute is the presentation and discussion of scientific and technical papers, but from early times it has been appreciated that great value can result from the personal contacts made possible by the inclusion in the programme of a number of social gatherings. Nor has this been confined to the United Kingdom, for on several occasions the Autumn Meeting has been held on the Continent, thus giving members an opportunity of meeting overseas members in their home country. Contact with other countries has been maintained, too, by the good offices of Corresponding Members in the countries concerned.

As early as 1910, the Institute realised the value of taking a broad view of the scientific background of its field of interest, and founded the annual May Lecture, which has been presented by many of the country's leading scientists. The demand later arose for an annual lecture to review some branch or aspect of the practical or industrial side of the non-ferrous field, and since 1922 a lecture of this type has been given at the Autumn Meeting.

A further valuable activity of the Institute has been the establishment of Local Sections and co-operation with independent provincial metallurgical societies. Not only do these afford members an opportunity of more frequent meetings, but the representation of Local Sections on the Council of the Institute is of mutual benefit.

One of the most profitable—as far as tangible results

are concerned—of the Institute's undertakings during the last fifty years has been the work of the Corrosion Research Committee, which was set up in 1910. This was primarily concerned with condenser tube corrosion, and as a result of the investigations of G. D. Bengough, R. May, and others, the serious troubles encountered in the Royal Navy were largely overcome, so that Mr. Churchill could say in 1940, comparing the two world wars "... one always expected a regular stream of lame ducks from the fleets to the dockyards with what was called 'condenseritis,' or heated bearings, or other mechanical defects. But now they seem to steam on for ever." The work of the Corrosion Research Committee under G. D. Bengough and J. M. Stuart also dealt with the corrosion of aluminium alloys, and this led to the development of anodic oxidation as a means of protecting them from corrosion.

Throughout its history, the Institute has been well served by a succession of able Presidents, Vice-Presidents and Members of Council, who, in turn, have been both guided and supported by an excellent staff, headed successively by Mr. G. Shaw Scott, Secretary from 1908 to 1944, and Lt.-Col. S. C. Guilan, who joined the staff in 1911 and was appointed Secretary in 1947, after an interregnum due to the war. In wishing the Institute every success, we have every confidence that the future will bring forth the men to maintain the progress which has been a feature of the first fifty years.

### Index to Scientific Journals

METALLURGIA is among the 510 periodicals that are being indexed by subject and author in a new publication announced recently. The primary subjects included in these indexes are solid state physics, nucleonics, radiation, optics, mechanics, astrophysics, radio, electronics, sound, astronomy, rockets, guided missiles, artificial satellites and space travel. These indexes, comprising several hundred thousand entries, have been compiled by the Library of the U.S. Naval Research Laboratory. The original index cards are to be reproduced in book form by offset printing, 21 cards per page, 10 × 14 in. Author and subject sections, and the monthly, quarterly and annual supplements to each, can be purchased separately.

The publication will be available only to those who subscribe in advance of printing, which will start in the third quarter of this year. The publication is offered by Micro-Photography Co., 97, Oliver Street, Boston, 10, Massachusetts.

### School of Welding Technology

THE first series of Courses organised by the School of Welding Technology between October 1957 and March of this year were very well supported, in two cases more than 100 applications being received for the 40 available places. A further six Courses have been arranged for the period April–September 1958, and again the number of participants will be limited to 40. Each five-day Course lasts from Monday to Friday, beginning at 11 a.m. on Monday and ending at 4 p.m. on Friday. Further details and enrolment forms can be obtained from the Secretary, Institute of Welding, 54, Princes Gate, Exhibition Road, London, S.W.7.

# Liquefied Petroleum Gases for Controlled Atmosphere Production

By L. G. W. Palethorpe, F.R.I.C., F.I.M.

Chief Metallurgist, Wild-Barfield Electric Furnaces Ltd.

*Liquefied petroleum gases are finding increasing application for the production of controlled atmospheres for heat treatment furnaces. The fact that they can now be supplied in bulk has led to their application in a number of large-scale heat treatment installations, and in this article the author discusses their properties and the ways in which they can be used for such operations as clean hardening, carburising, carbonitriding and bright annealing.*

UNDOUBTEDLY, one of the major post-war developments in the heat treatment field is the use of controlled atmospheres for the carrying out of processes ranging from scale-free annealing and hardening to gas carburising and carbonitriding. Suitable furnaces and atmospheres have been developed for most of the treatments involved in the processing of both ferrous and non-ferrous products, and today, the engineering and metallurgical industries widely accept and use them.

For most applications, the source of these atmospheres is a fuel gas which is either partially burned or cracked with air, followed by purification where necessary. In this country, the fuel gas most widely used for these purposes is town gas, but in certain applications, it involves disadvantages. These do not arise in the United States, because of the ready availability of naturally-occurring methane gas, and where they do occur in this country, increasing availability of liquid petroleum gases and their development for industrial purposes may help to overcome them.

## Liquefied Petroleum Gases

The term liquefied petroleum gas is used to describe any product which consists of one or a mixture of the hydrocarbons propane, propylene, butane, and butylene—often referred to as L.P. gases. Although they have been firmly established for some years in the U.S., where

they are derived from natural gas, it was not until 1934 that L.P. gases were first marketed in this country. However, by 1939, their use had become fairly widespread. Butane was used for domestic heating while propane was used in industry, and both gases were distributed in cylinders with a maximum capacity of 120 lb. Since then, with the post-war expansion of the U.K. refineries, increased quantities of L.P. gases have become available as a source of heat. The latest and most important development came in 1954, when the first bulk delivery to an industrial user, consisting of 4 tons of propane, was made in a specially designed vehicle. Today both propane and butane can be obtained freely in this manner or in small quantities as required.

Since the L.P. gases marketed in this country are normally mixtures of hydrocarbons, it follows that in order to maintain a high and uniform standard of quality some form of control is required. To meet this, a manufacturing specification has been drawn up by the Liquefied Petroleum Gas Industry Technical Committee, and this covers the essential properties to which the refineries manufacture their products.

The properties of commercial propane and butane which are of concern to those engaged in controlled atmosphere production are contained in Table I. They are similar in many ways, as might be expected from the close chemical relationship of the two compounds, but they differ essentially in their boiling points and con-

TABLE I.—AVERAGE PROPERTIES OF COMMERCIAL BUTANE AND COMMERCIAL PROPANE

	Butane	Propane
Specific gravity of liquid at 60° F. . . . .	0.570-0.580	0.500-0.510
Specific gravity of gas compared with air at S.T.P. . . . .	1.90-2.10	1.40-1.55
Latent heat of vaporisation at 60° F. (B.Th.U./lb.) . . . . .	160	154
Volume of gas per 1 lb. of liquid at S.T.P. (cu. ft.) . . . . .	6.5-6.9	8.6-8.7
Specific heat of liquid (B.Th.U./lb./°F.) . . . . .	0.57	0.60
Limits of inflammability (% gas and air to . . . . .	Upper 9	10
form a combustible mixture) . . . . .	Lower 1.5	2
Gross calorific value (B.Th.U./lb.) . . . . .	21,300	21,500
Gross calorific value (B.Th.U./cu. ft.) . . . . .	3,200	2,450
Sulphur content (%) . . . . .	Negligible to 0.01	Negligible to 0.01
Boiling point (°F.) . . . . .	20	-40
Imperial gallons per ton at 60° F. . . . .	385	448
Therms per ton . . . . .	477	480
Vapour pressure (for products of the maximum specified vapour pressure) (lb./sq. in. absolute) at . . . . .	-40° F. . . . .	15
	0° F. . . . .	35
	32° F. . . . .	75
	100° F. . . . .	225
Air required for combustion (cu. ft. of air to burn 1 cu. ft. gas) . . . . .	113° F. . . . .	270
	31	24
Ratio of gas volume to liquid volume at S.T.P. . . . .	240	275

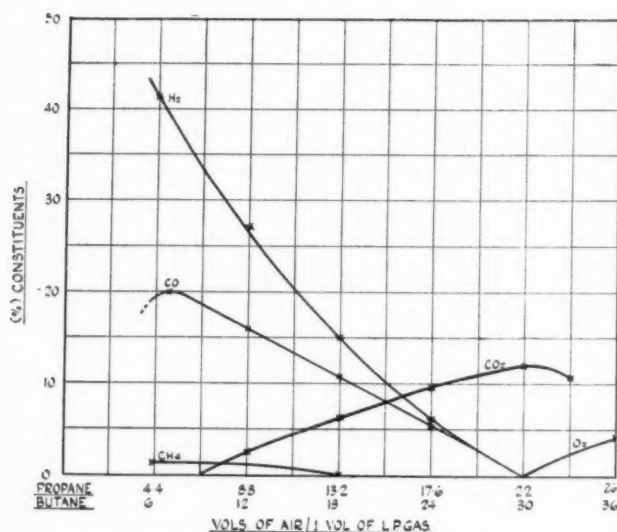


Fig. 1.—Air/gas ratio chart for propane and butane.

sequently in their vapour pressures. Resulting from this, butane usually requires the assistance of a vaporiser in handling, except during the warmer weather. This, together with the metallurgist's preference for propane as an enrichment addition to certain controlled atmospheres, tends to make this compound the more popular choice as the raw material for atmosphere production.

#### Advantages of Liquefied Petroleum Gases for Atmosphere Production

The principal advantages of L.P. gases for atmosphere production are low sulphur content, purity, and consistency of properties.

Although the maximum quantity of sulphur is specified as 0.02%, it is usually of the order of 0.003 to 0.004%. This low sulphur content is extremely important from the metallurgical point of view for two reasons. First, the effect of this element, especially in the presence of hydrogen, can be disastrous on heat resistant alloys at elevated temperatures—nickel-chromium muffles, furnace fur-

niture, and heating elements all suffer from serious attack in a relatively short time. Second, the presence of sulphur interferes with the efficient working of the controlled atmosphere. For example, in the annealing and sintering of copper alloys it causes staining, due to the formation of a film of black copper sulphide on the work.

L.P. gases do not contain variable quantities of carbon dioxide, oxygen, or water vapour, nor do their principal constituents vary in quantity. Thus, when a controlled atmosphere is required for a particular purpose, the conditions of operation can be pre-determined with the knowledge that they will not require to be varied once the generator is running in production. This is particularly important for gas carburising, in which process close control of atmosphere composition and dew point with minimum supervision is essential.

In regard to cost, it must be remembered that L.P. gases are high in purity and calorific value as well as consistent in quality, so that the apparently high cost may be misleading. For example, 1 volume of propane requires 7.5 volumes of air for reaction and produces 13 volumes of endothermic gas, whereas 2 volumes of town gas require approximately 1 volume of air and produce 3.3 volumes of endothermic gas. If, therefore, it is required to produce, say 1,000 cu. ft. per hr. of endogas from town gas, then approximately 620 cu. ft. or 3.1 therms will be needed at an hourly cost of 4s. 5d., assuming that town gas costs 1s. 5d. per therm. Using commercial propane as an alternative, it would require 8.7 lb. or 1.84 therms at a cost of 2s. 9d. per hour, assuming the cost of propane to be 1s. 6d. per therm. This would show a considerable annual saving on a generator which is working continuously. It must be remembered, however, that the above figures are based on the use of sufficient gas to warrant the purchase of bulk loads of 4 tons or more of L.P. gas delivered into storage tanks. The use of smaller quantities would be

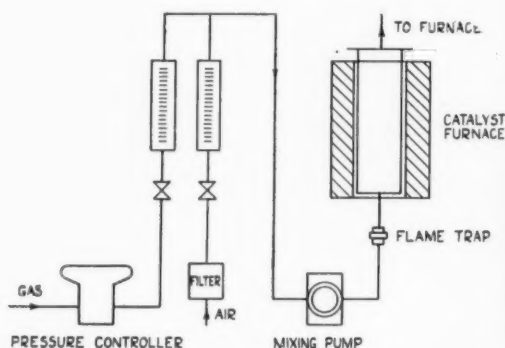


Fig. 2.—Simple flow diagram for endothermic generator.

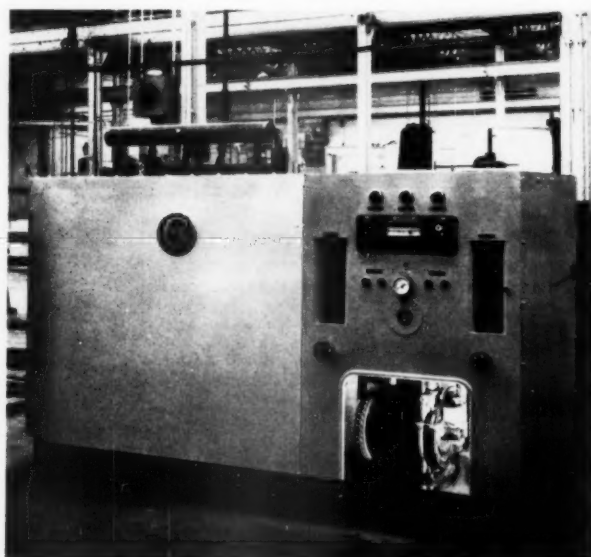


Fig. 3.—Endothermic generator, 1,000 cu. ft. per hour.



proportionally dearer, though they would give certain benefits of purity and consistency.

### Types of Controlled Atmosphere

The principal types of controlled atmosphere which may be prepared from L.P. gases are of an endothermic and exothermic nature, respectively, and are so named on account of their method of manufacture. By the combustion or reaction of the gas and air in varying proportions, a wide range of resultant gas compositions may be obtained. At ratios up to about 25% complete combustion, i.e., up to about 7 l air to propane, insufficient heat is generated to maintain the reaction temperature. Therefore, the chamber must be heated externally, and although a little heat is given out the process is said to be endothermic. Furthermore, in order to promote completion of reaction, the chamber is filled with a catalyst over which the gas/air mixture must pass. At ratios from about 70% to almost complete combustion—14 to 21 l air to propane—the heat of reaction is ample to maintain the reaction chamber at the required temperature and the process is said to be exothermic. An indication of the range of gas compositions which can be obtained under the various reaction conditions is given in the diagram shown in Fig. 1, and a description of each type of generator and the uses to which its product gas can be put are given in the following paragraphs.

### Endothermic Atmospheres

In the case of endothermic atmospheres, the generator consists of either one or more cylindrical retorts, in which is placed the catalyst material, usually in the form

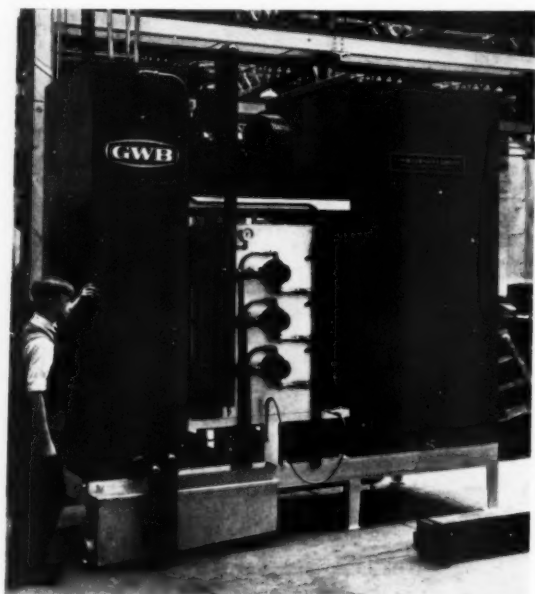


Fig. 5.—Exothermic generator, 3,000 cu. ft. per hour.

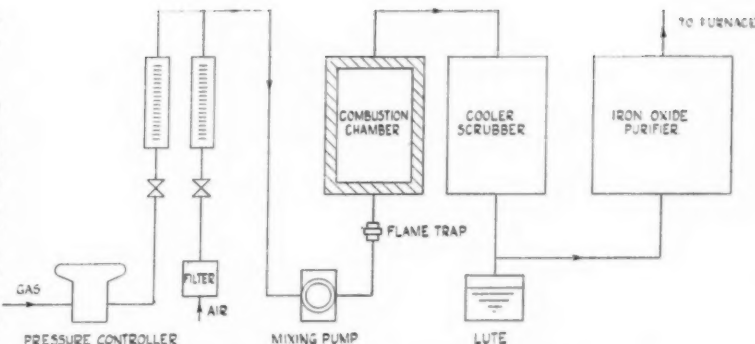


Fig. 4.—Simple flow diagram for exothermic generator.

of pellets about  $\frac{3}{8}$  in. diameter. The retorts are heated externally to about 1,000–1,050° C. by either electric elements or radiant tube gas burners. The gas and air are measured by means of direct reading flowmeters and are mixed and pumped through the retorts. The product gas is led off from the top and fed to the furnaces requiring it. Fig. 2 illustrates diagrammatically the flow of gas through the generator, and Fig. 3 shows a photograph of a typical plant.

As may be seen from the diagram in Fig. 1, endothermic atmospheres consist principally of carbon monoxide, hydrogen and nitrogen. The impurities which are of importance to the metallurgist are carbon dioxide and water vapour. Both are present in small quantities only (up to 0.5% CO<sub>2</sub> and dew point 0° to 30° F.) but their concentrations increase with increasing air/gas ratio, whereas the hydrocarbon content decreases. This gives a measure of control of carbon potential of the atmosphere which, together with its highly reducing nature, makes possible the clean heat treatment of medium and high carbon steels with excellent results. Examples of typical operations include the clean hardening and bright annealing of medium and high carbon steels, the restoration of carbon in decarburised components, brazing and sintering, and gas carburising. In some of these processes, where the carbon potential required is high—in gas carburising and the treatment of high carbon steels—it may be necessary to enrich the atmosphere a little with propane, but further reference to this will be made later.

### Exothermic Atmospheres

In the case of exothermic atmospheres, the generator consists of a refractory-lined combustion chamber into which is fed the requisite air/gas mixture measured by means of flowmeters. The product mixture is cooled to remove the water formed during the reaction. Reference to Fig. 1 will show the range of composition obtainable by varying the air/gas ratio, but in addition there will be present about 2% water vapour, the exact amount varying with the ambient temperature of the cooler. For most applications, exothermic atmospheres are used without removal of this residual water vapour, but should its presence be deleterious for any particular application, it may be removed by the normal silica-gel or alumina drying equipment. Fig. 4 illustrates diagrammatically the layout of an exothermic generator, and Fig. 5 is a photograph of a typical plant.

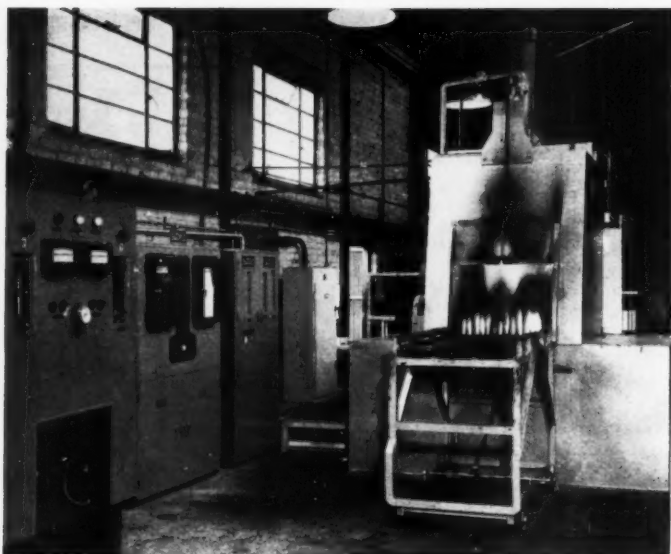


Fig. 6.—Wild Barfield "Ace" horizontal sealed quench furnace.

Exothermic gas is neutral to slightly reducing, dependent on the air/gas ratio, and may be used for the heat treatment of low carbon steels and some non-ferrous metals and alloys. In the case of steels, the rich end of the ratio must be used in order to promote the formation of carbon monoxide and suppress the formation of carbon dioxide. Too much of the latter may cause oxidation at treatment temperatures. In the case of non-ferrous alloys such as copper and nickel, the lean end of the ratio is used so that the atmosphere is principally a nitrogen-carbon dioxide mixture. Sulphur content must be kept low to avoid staining, but this is more easily achieved when generating the atmosphere from L.P. gases.

There are some applications which call for an atmosphere completely inert to the metal being treated, and at the same time free from explosion risks. This set of conditions is most likely to be called for in large continuous furnaces and, when it is the obvious choice is nitrogen, which may be produced from exothermic gas.

The technique employed is to adjust the generator to give a minimum carbon monoxide content by using almost full combustion conditions. The product gas consists of nitrogen and carbon dioxide, of which the latter is removed by "stripping" in one of the organic amine solutions.

The plant for this consists of a tower filled with refractory rings through which the burnt gas is passed and into which the active amine solution is sprayed. The carbon dioxide absorbed by the amine solution is removed in regenerative boilers. Finally, if the gas is required dry, the water vapour may be removed in a conventional regenerative-type dryer unit.

"Stripped" gas is almost pure nitrogen, but should operating conditions warrant it, small amounts of carbon monoxide and hydrogen may be retained by suitable adjustment of the air/gas ratio. It is extremely useful for treatment of most ferrous and non-ferrous alloys, and although the initial cost is relatively high, the exogas and "stripper" system is the cheapest method of producing large quantities of nitrogen as a furnace atmosphere.

## Endothermic Gas Enrichment

Probably one of the oldest uses of L.P. gases in furnace atmosphere practice is for the enrichment of endothermic atmosphere in the gas carburising process, and nowadays the same technique is used in the carbonitriding process. The endothermic gas, which has a carbon potential of about 0.6, is used as the neutral carrier, and small additions of propane are accurately metered into the furnace to raise the carbon potential to the requisite level.

In modern gas carburising plant, particularly the larger batch-type and the continuous furnaces, the control of carbon potential has been taken a stage further by automatic control equipment. If it be so desired, the control may be exercised by admitting a carrier gas of controlled dew point into the furnace and then automatically metering a controlled addition of propane according to the dew point reading in the carburising zone.

## Atmosphere Controlled Furnaces

Considering atmosphere controlled furnaces, the range of endothermic and exothermic atmospheres described may be used for the majority of heat treatment operations with the exception of stainless steels, Nimonic alloys, and most of the "newer" metals. The types of furnaces used are diverse: depending on production and economic requirements, both horizontal and vertical batch types, including bell furnaces are used, as well as pusher, mesh belt, shaker hearth, and other types of conveyor furnace.

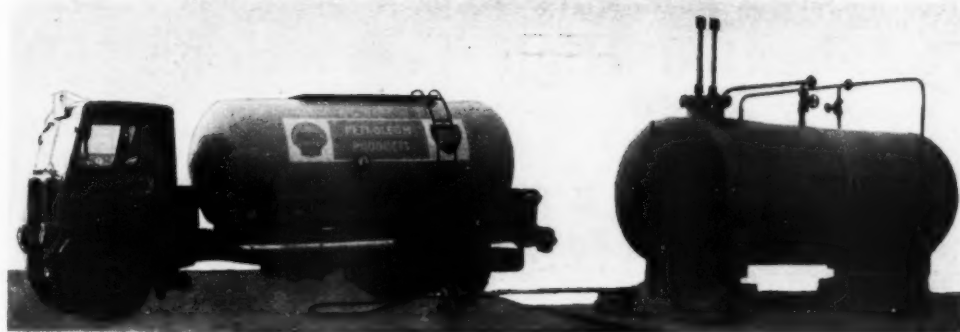
In the batch-type section, one of the most interesting developments in recent years is the horizontal sealed quench furnace, as illustrated in Fig. 6. It consists of a horizontal furnace chamber fitted with a fan in the top. On the front is a purged quench chamber designed so that the charge may be handled without contact with air when it is hot. The method of operation is as follows:—

A basket-load of work is placed into the quench chamber on the roller platform provided and the outer door is closed. The quench chamber is automatically purged with atmosphere flowing from the furnace. When purging is completed, the inner furnace door may be raised and the charge is pushed inside. When the requisite heating cycle has been completed, the inner furnace door may be raised again and the charge is pulled back on to the roller platform in the quench chamber and the inner door is again closed.

Now the charge is lowered into the oil tank below and quenched. At this stage, the outer door may be opened and the next cycle commences. The charge in the oil may be removed at a convenient time during the next heating cycle. This type of furnace may also be provided with a water-jacketed section at the top of the quench chamber into which work may be raised for slow cooling in atmosphere controlled conditions. Thus, in one furnace, a range of operations including clean hardening, gas carburising, carbonitriding, and bright annealing may be carried out.

A very important point about atmosphere controlled furnaces is that no matter how good is the atmosphere

Fig. 7.—Typical 5-ton propane storage tank and vehicle used for delivering 4-4½ ton loads of L.P. gas.



that enters the furnace, it will be of no avail unless the latter is properly designed. It is the quality of the atmosphere within the furnace that matters as far as the process is concerned. A perfect atmosphere fed into a poor furnace, or into a good furnace poorly maintained, is a waste of time and money. Thus, the design of the furnace and its operation and maintenance must be considered just as carefully as the atmosphere to be employed.

#### Storage of L.P. Gases

The storage and handling of the L.P. gases is outside the scope of this article, but it may be stated briefly that the cheapest way to buy L.P. gases is in deliveries of

4 tons or more at a time, in which case bulk storage tanks must be installed (Fig. 7). Should requirements not warrant such an installation, 1 ton demountable skid tanks may be used and returned to the refinery for filling. On a smaller scale still, 100 lb. cylinders may be used, and in this case, for continuous consumption, it is advisable to have two banks of cylinders with an automatic change-over device.

#### Acknowledgment

In conclusion, I should like to acknowledge the assistance accorded to me in the preparation of this article by Mr. C. F. Port, and Bottogas, Ltd.

## Molybdenum-Base Alloys

A FOUR-YEAR investigation of molybdenum-base alloys prepared by powder-metallurgy methods was summarised late last year by Robert I. Jaffee of Battelle, before the Symposium on Molybdenum of the Office of Naval Research. The investigation, conducted at Battelle, led to considerable knowledge about the properties and advantages of the alloys, as well as about the mechanisms for producing them.

Jaffee pointed out that the major difference between the best molybdenum-base alloys prepared by powder-metallurgy as compared with arc-casting methods is the superior hot breakdown fabrication characteristics of the former product. The underlying reason for this difference appears to lie in the finer initial grain size of the as-sintered powder-metallurgy alloy, and the fact that the impurities are distributed over a much larger grain-boundary area, thus making their presence innocuous. The room- and elevated-temperature strengths of the best molybdenum-base alloys prepared by powder-metallurgy methods are equivalent to those of the best arc-cast alloys. However, because of the higher oxygen contents usually found in powder-metallurgy-produced materials, the ductility of thin weldments is inferior to that of arc-cast alloys.

Initially, powder-metallurgy alloys made with conventional alloying additions were studied. The most effective alloying addition was silicon. Significant improvements in strength at room and elevated temperatures could be achieved with silicon alloy contents of the order of 0.1-0.2%. Chromium also was found to be a good conventional alloying addition; 1-2% may be added. These amounts improve room- and elevated-temperature strength and increase the recrystallization temperature range. Cobalt was found to have a high

strengthening effect, but lowered the recrystallization range. The addition of tungsten resulted in alloys with excellent mechanical properties and improved recrystallization characteristics, but tungsten had the lowest specific strengthening effect of any alloying addition and was not advantageous from a strength-weight point of view.

A new type of alloying addition to molybdenum was discovered in this research, in which the addition of stable oxides produce dispersion hardening. The most suitable oxides were those which were available in the finest particle size, had high hardness, high stability, and high modulus of elasticity. The oxides of zirconium and titanium were most effective, with chrome oxide good, but somewhat less effective.

The optimum alloys produced by arc-casting methods are those containing titanium or zirconium, the same elements which were found to be most effective when added as oxide dispersions to powder-metallurgy molybdenum alloys. It was concluded that the mechanism for improvement in elevated-temperature strength was similar in both cases, part of the metallic alloy addition in the arc-melted alloys being oxidized during melting to produce fine dispersions of oxide.

The economic differences between arc-cast and powder-metallurgy molybdenum products are important. Thus, if advantage is taken of furnace sintering procedures, there will be almost no scrap generated in the primary breakdown operation of powder-metallurgy alloys. In the case of arc-cast alloys, on the other hand, the end losses in extrusion are inevitably high. However, if true hot-working procedures make a direct hot breakdown operation feasible for arc-cast alloys, the economic advantage disappears.

# Accelerated High Temperature Oxidation due to Vanadium Pentoxide

By K. Sachs, M.Sc., Ph.D., A.I.M.

G.K.N. Group Research Laboratory, Wolverhampton.

*Gas turbines running on residual oils from the distillation of crude oils would be an economic proposition in many marine and land-based applications, but trouble is experienced in the case of oils from several sources in that such oils are rich in a corrosive ash, which clogs up the turbine and attacks metal components operating at high temperatures. This phenomenon has been attributed to the vanadium pentoxide in the ash, either alone or in combination with other substances, and in this article the author discusses the problem in the light of the results of a number of investigations.*

(Continued from page 173 of the April issue)

## Possible Remedies

A variety of methods has been suggested for overcoming the problem of catastrophic corrosion by vanadium pentoxide: they reflect the difficulties of the problem itself. Metallurgists demand a fuel free of vanadium, oil technologists suggest that corrosion resistant alloys should be developed, and both combine to express the pious hope that some additive will be found—cheap, easily available, soluble in oil, having no deleterious effects on other properties—which would render vanadium pentoxide harmless. The obvious solution is a fuel oil containing no vanadium; the oil industry is anxious to supply such a fuel, indeed its main income is derived from the sale of such fuels, but the price is too high. In fact, even the use of residual fuel oils derived from vanadium-free crude is only possible in geographically favoured areas; heavy transport costs make the general use of such oils uneconomic.<sup>2</sup>

It is possible to reduce the ash content of residual oils by centrifuging, when sediments and suspended solids are removed.<sup>2</sup> Unfortunately, vanadium originally present in the oil as a soluble organic compound is oxidised during combustion and enters the ash as a solid product of combustion; centrifuging therefore concentrates vanadium pentoxide in a smaller total ash content, as is shown by experimental figures quoted in Table VI. In practice, this may still be beneficial, because there is less ash to deposit on metal surfaces. There is a tendency to write specifications in terms of the content of vanadium pentoxide in the ash rather than the oil; this might give the oil supplier an incentive to add some innocuous solid to dilute the ash rather than to centrifuge the oil.

Other chemical treatments to remove the organic vanadium content from the residual oil are theoretically possible; in essence they involve treatments similar to the catalytic cracking which forms part of normal refining practice. If such treatments were an economic proposition, they would be used to increase the yield of

distillate fuels. It can be concluded that these methods are impracticable within the price limitations imposed on residual oils.

A more promising approach would be the removal of the ash after the oil has been burnt, by some form of separator between the combustion chamber or flame tubes and the turbine. This would involve a serious loss of heat and, therefore, of efficiency, and would present extremely difficult design problems. The matter is discussed in detail by Hughes and Voisey<sup>15</sup> whose comments are quoted extensively below:—

“A survey of the possible ways of securing an ash-free stream of air to the turbine suggests that none of the ash collector systems so far developed can be relied upon to deal with a wide range of fuels. The trouble is that at gas-turbine temperatures the ash is sometimes dry, sometimes sticky, and the “volatile” ashes (e.g. sodium and potassium) may pass over in an extremely fine state after sublimation in the combustion flame . . .

“It would seem that a dry ash could be satisfactorily collected by such mechanical means as centrifugal collectors, aerodynamic collectors and electrostatic cleaners. Attempts to collect sodium ash in an experimental turbine with a centrifugal collector were, however, not successful, even with cooled walls. It is necessary to use the smallest size of cell to get efficient collection of small particles, and a collector for a large plant would therefore consist of many cell units in parallel. The battery would not be cheap, and the aerodynamic design would call for careful attention.

“The term ‘aerodynamic collector’ is used here to describe systems which take advantage of the flow pattern round cascades of blades. Collection by impingement offers one possibility in theory, but results of tests made by the authors were not encouraging, possibly because they were conducted with sodium ash. By using highly cambered blading, the ash may be rejected instead of collected by the blades, as in the

TABLE VI.—EFFECT OF CENTRIFUGING TO CONCENTRATE THE VANADIUM PENTOXIDE IN A SMALLER ASH CONTENT

	Refinery					
	A		B		C	
	Before	After	Before	After	Before	After
% Ash in Fuel Oil . . . . .	0.057	0.036	0.055	0.048	0.035	0.011
% $V_2O_5$ in Ash . . . . .	7.9	13.4	56.5	65.0	11.1	27.5
% $V_2O_5$ in Oil . . . . .	0.0047	0.0048	0.0311	0.0312	0.0039	0.0020

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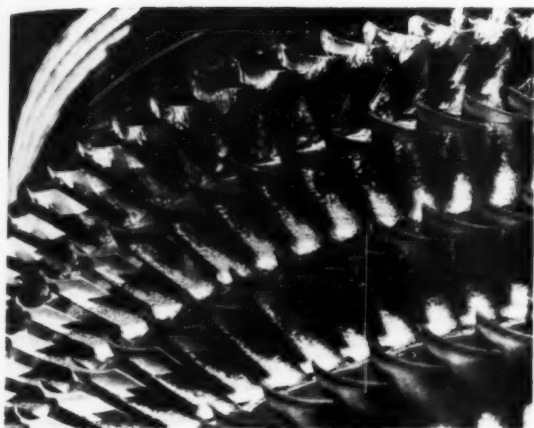


Fig. 30.—Turbine spindle blades after injection of water during test.<sup>15</sup>

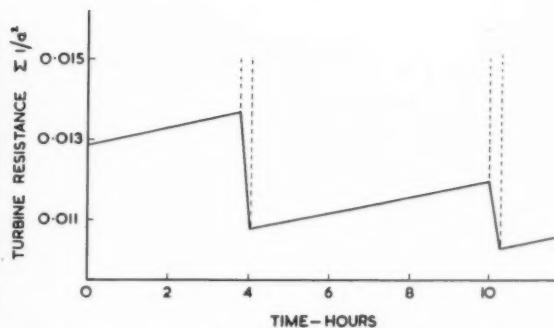


Fig. 31.—Effect upon turbine resistance of water injection using oil: broken lines indicate 15 minute periods of water injection (0.3 lb. water per second).<sup>15</sup>

Systeme Lindenrothe. This is an enrichment system whereby the ash is concentrated into a smaller quantity of gas. Although it demands a fan to deal with this hot gas, and auxiliary cleaning apparatus to extract the solid matter before the gas is returned to the main stream, it is very attractive in theory. It offers promise of being more compact and efficient than a multi-cell centrifugal separator.

"Some tests are in hand with electrostatic cleaning, but no results are available to date (1949). Such plant must be large because of the low throughput velocity, and it remains to be seen whether the process can be made to work at 1,200° F.

"It seems likely that the mechanical collection system will not deal with all the alkali-metal ash, and in particular with that portion which is sublimed from the dry-ash fraction in the flame. It is possible that a refractory matrix placed in the hot gas stream after a battery of mechanical collectors would complete the process if it were cleaned often, so that there was no risk of the ash re-subliming into the gas stream. The matrix would operate as a surface trap and would need a generous surface area to length ratio. Using refractory-lined combustion chambers and pipes is a rather clumsy approach on the same lines.

"The logical end to such schemes might be a viscous-type filter, and such a filter has proved to be very successful in cleaning the air supplied to the compressor of the experimental gas turbine. Again, the cleaning would have to be frequent, and this is a mechanical design problem.

"The degree of cleaning to which the mechanical collection should proceed before collection by the matrix is started, would follow from economic and operating conditions. The refractory matrix might be objectionable in gas-turbine schemes using waste-heat exchangers, because it would be expected to catalyse the sulphur dioxide to sulphur trioxide transformation.

"In the absence of gas-cleaning means, some of the palliative measures used in the authors' experimental gas turbine may be of interest.

"The simplest procedure is to shut down the turbine and rely upon thermal shock to crack off the deposit.

"Another method, that of running alternately on

ashing and non-ashing fuels, depends for its success on the nature of the ash. With soluble ashes the turbine may be washed out while running. Fig. 30 shows the appearance of the turbine after being sprayed for 15 minutes with 0.3 lb./sec. water flow (25% of the air flow), and Fig. 31 shows the effect on the turbine resistance. The essence of the method is to use a large quantity of water in a short time so that solution occurs before evaporation. Similarly, the spray should not be too fine. In these tests there were no signs of erosion, presumably because the mechanism of condensation of large drops on the blades which occurs in low pressure steam turbines was not present in the gas turbine. Because tap water was used, a light deposit of calcium salts was left on the blades."

It seems probable that ashes rich in vanadium pentoxide would greatly increase the already prohibitive difficulties of cleaning the hot gases or washing the ash deposit off the blades. The gas cleaning installation would be subject to severe oxidation or fluxing, while the deposit on the blades would contain products of oxidation in such quantity that it would be substantially insoluble in water.

A great deal of work has been done in attempts to find a cheap additive which would render the vanadium pentoxide harmless. Reference has already been made to the addition of carbon tetrachloride to the fuel of an experimental closed-cycle turbine<sup>6</sup> in the hope that volatile vanadium chloride would form and would disappear through the exhaust system; in fact there was combined attack by vanadium pentoxide and chlorine on the heat exchanger tubes, and corrosion was correspondingly severe. Experiments have also been made with antimony trioxide additions;<sup>25</sup> it is known that the catalytic activity of vanadium pentoxide in the industrial oxidation of sulphur dioxide can be inhibited by arsenic poisoning of the catalyst, and antimony trioxide is chemically very similar to arsenious oxide. Unfortunately, a corrosion test on a complex austenitic steel for 100 hours at 700° C. showed that up to 5% Sb<sub>2</sub>O<sub>3</sub> did not result in any significant reduction in attack.

In most other cases, the task ascribed to the additive was the formation of a high-melting compound with the vanadium pentoxide, so that the fluxing mechanism, which appears to be closely associated with catastrophic oxidation, could not operate. In one typical investigation,<sup>28</sup> the approximate melting points of a synthetic ash diluted with increasing amounts of the oxides of mag-

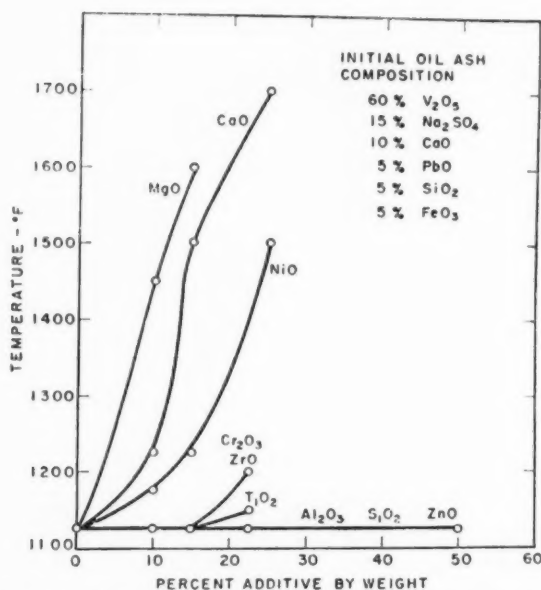


Fig. 32.—Effect of increasing weights of various oxides on the melting point of a typical crude oil ash.<sup>25</sup>

nesium, calcium, nickel, zirconium, chromium, titanium, zinc, aluminium and silicon were determined. The results, illustrated in Fig. 32, show that only the oxides of magnesium, calcium and nickel increase the melting point of the ash to an appreciable extent. Cylindrical specimens were cut from  $\frac{3}{8}$ -in. diameter bar stock of a molybdenum-bearing austenitic steel (type 316), and a  $\frac{5}{16}$ -in. diameter hole was drilled in the top face. The three "beneficial" oxides, magnesium oxide, calcium oxide and nickel oxide, were mixed individually with the synthetic ash and about 2g. of the mixture could be packed into the specimen cavity. The time required to give a 20% increase in weight is plotted against the temperature in Fig. 33. At the high temperatures employed in this work, pure vanadium pentoxide gave slightly more severe attack than the synthetic ash, while 25% additions of the various oxides had a profound beneficial effect. The addition of magnesia to synthetic ashes was also shown to be beneficial in experiments with various laboratory atmospheres.<sup>10</sup> In another study,<sup>25</sup> various additions of magnesium oxide, aluminium oxide, kieselguhr, vermiculite and zinc oxide, were made to a corrosive mixture of vanadium pentoxide and sodium sulphate. "Batches of weighed quantities of ash mixture (90% V<sub>2</sub>O<sub>5</sub>, 10% Na<sub>2</sub>SO<sub>4</sub>) and the additives to be tested were roughly mixed by stirring with a spatula and then brought into intimate contact by grinding in a mortar and pestle. Cylindrical metal corrosion specimens of known weight in silica crucibles were covered with the powdered mixtures and placed in an electric muffle furnace. Tests were carried out at 700° C. for 100 hours and, during the majority of the tests, sufficient air was passed through the furnace to change the furnace atmosphere every few minutes. After cooling, the specimens were descaled by the sodium hydride process and re-weighed.

The results of these tests, some of which are shown graphically in Fig. 34, indicate that with the exception of magnesium oxide and vermiculite (the latter on two of

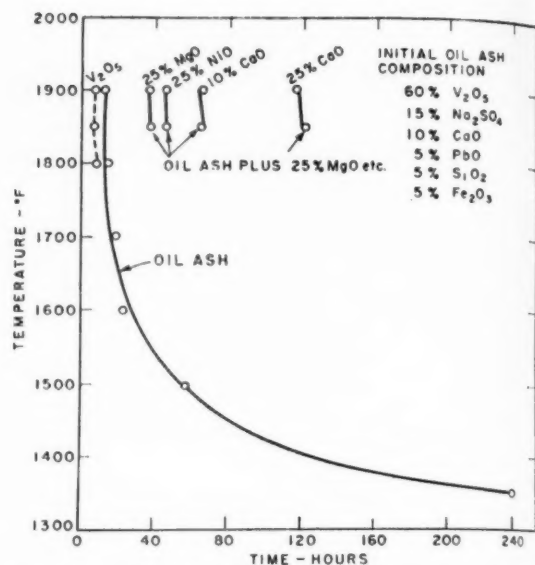


Fig. 33.—Effect of various oxides on the time for 20% gain in weight of Type 316 stainless steels.<sup>28</sup>

the three alloys tested only) these additives are capable of bringing about a marked increase in the amount of attack at certain proportions. In Figs. 35a and b, this effect is shown for kieselguhr and zinc oxide-ash mixtures on G.18B, and compared with the straightforward behaviour of magnesium oxide in Fig. 35c. Apart from this peculiarity, however, all the additives tested were effective in reducing corrosion when employed in sufficiently high concentration: zinc and magnesium oxides were especially effective.

"It was noticed that those additions which brought about a marked reduction in corrosion also produced non-molten ashes which did not readily adhere to the metal specimens. With increasing dosages, this dryness proceeded through the stage of friable solids in which the fused ash was acting rather like a cement to that of truly free-running powders. Of the compounds investigated, silica, in the form of kieselguhr, seemed to be the least effective from this point of view, although it would be unwise to make any firm conclusions, as the experiments did not include an investigation of factors such as particle size range and previous history of the refractory powders. These variables were kept as constant as possible by using materials from the same source in each test. It can be concluded with some certainty, however, that the use of such additions to an ash will not only reduce corrosion, but should also be of some benefit in alleviating engine fouling; to what degree can be determined only by engine tests.

"When, in later experiments with alumina and vermiculite, air was not passed through the furnace, and corrosion proceeded in a still atmosphere, it was found that both the extent of and the critical concentration for increased attack were liable to variation.

"The results in Table VII show that the effect of a still atmosphere has been to reduce considerably the attack on G.18B with 1/1 vermiculite-ash mixture. The critical concentration for increased attack of alumina-ash mixture has been increased from a ratio of 2 : 1 to 3 : 1, or above, and the extent of the maximum attack

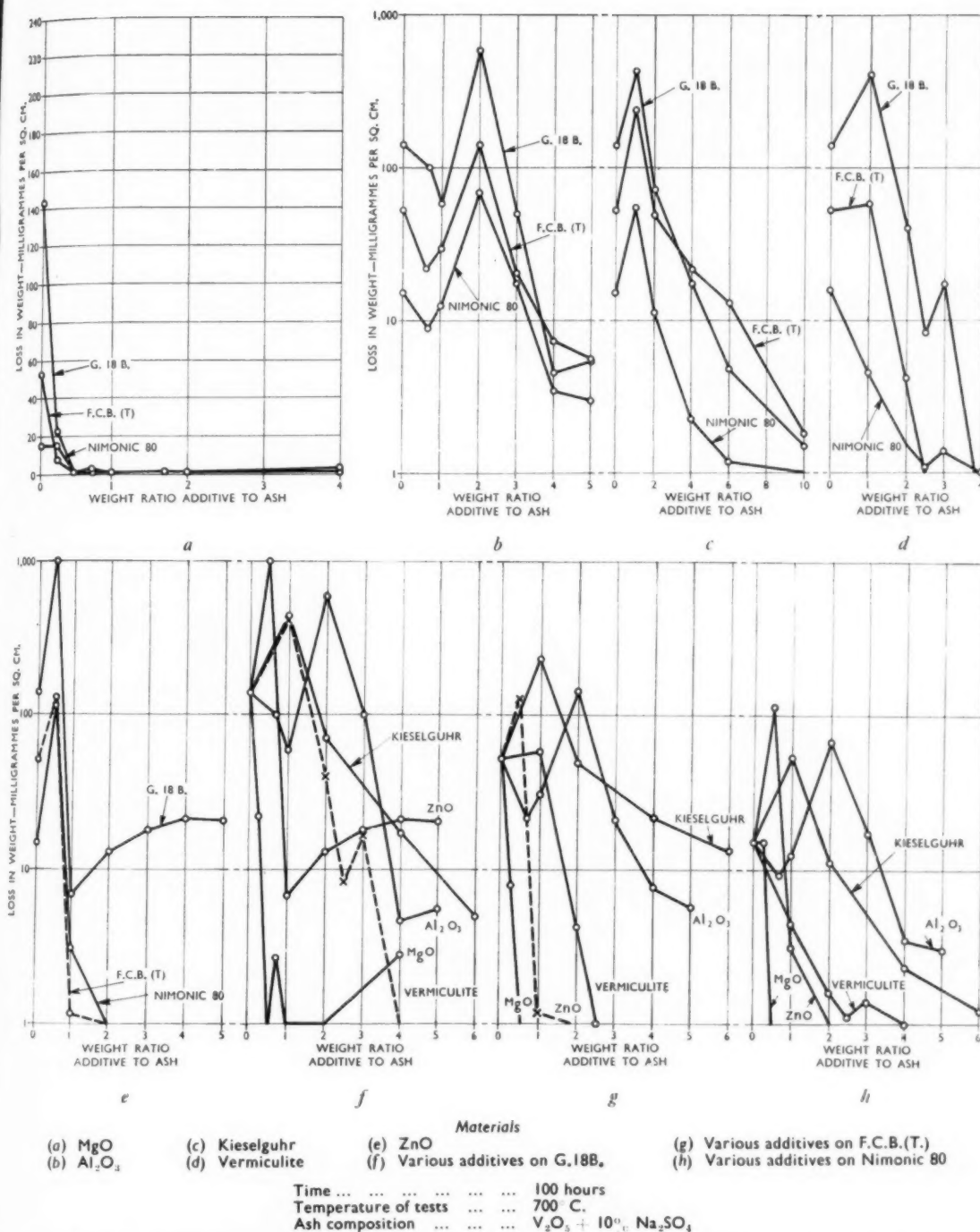


Fig. 34. Effect of various materials added in increasing quantities to a synthetic ash mixture on the scaling of three heat-resistant alloys.<sup>25</sup>

has been much reduced. With magnesium, this phenomenon of an increased attack at low proportions of oxide addition does not seem to occur, and the use of a still atmosphere in the furnace had little effect. This is shown in Table VIII.<sup>25</sup>

The determination of solidus temperatures in binary mixtures of vanadium pentoxide with various other oxides, by Lucas, Weddle, and Preece,<sup>23</sup> also had the object of finding suitable additives, but no oxidation tests were carried out. The curves show minima at

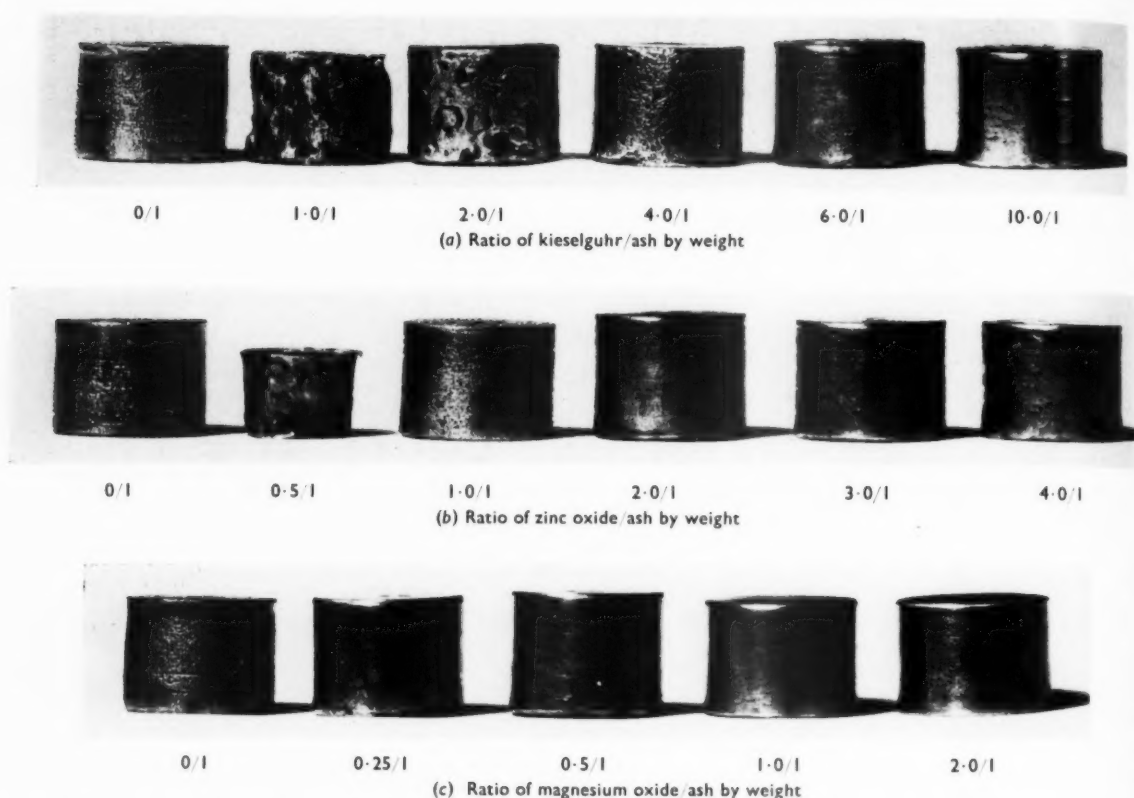


Fig. 35.— Effect of increasing concentrations of various materials added to synthetic ash on the corrosion of G.18B. Ash mixture : 90%  $V_2O_5$  + 10%  $Na_2SO_4$ . 100 hours at 700° C.; sodium hydride descaled.<sup>25</sup>

intermediate compositions, and this led the authors to conclude that substantial additions of refractory oxides would have to be made to ensure the absence of a liquid phase in the mixture, while small additions would lower the liquidus of the mixture and, therefore, presumably increase the severity of oxidation. The results of Frederick and Eden,<sup>25</sup> quoted and illustrated above, confirm this deduction.

The latter authors have extended their laboratory experiments to rig tests<sup>25</sup> at temperatures between 650 and 760° C., with magnesium and zinc oxides, using dosages of the order of twice the ash concentration in the oil. The suppression of attack is described as "very good," even where the fuel was also rich in sulphur. Nevertheless, the reduction in attack was invariably less than had been found in the laboratory tests; this is attributed to the reaction of sulphur trioxide in the gases with the basic oxides, lowering the effective concentration of the additive.

In the discussion of a paper describing the effect of refractory oxides on accelerated oxidation,<sup>28</sup> Slunder reports that the oxidation of boiler tubes due to vanadium in the ash of Bunker C oil was greatly reduced by dissolving a calcium soap in the oil; the inference is that calcium oxide was formed during combustion and inhibited oxidation.

There are no reports of the extensive use of refractory oxides in gas turbines. One important reason is the necessity of adding so much refractory oxide that

fouling is accentuated and serious erosion problems may arise.<sup>41</sup> If enough basic oxide has to be added to allow for the formation of sulphate by reaction with sulphur trioxide in the products of combustion, the total bulk of solid matter in the gas stream will be further increased.

In the absence of a satisfactory "miracle pill" which would render residual oils harmless at relatively little cost, the possibilities of metallurgical solutions must be considered. The response of high-temperature alloys to accelerated oxidation has been examined by a number of investigators,<sup>7, 16, 22, 40</sup> but no alloy has been found which is fully resistant. Nickel-base alloys are not quite such ready victims of the catastrophic oxidation caused by pure vanadium pentoxide as austenitic steels, but are more susceptible to sulphur penetration. The rapid sorting test developed by Fitzer and Schwab,<sup>40</sup> which has been described above, gave better results for many austenitic steels than for an 80/20 Ni-Cr alloy (Fig. 36); in view of the bulk of evidence to the contrary,<sup>6, 16, 23, 25</sup> this result can be regarded as a reflection on the validity of the test. It has been observed that the addition of 10 or 20% Co to an austenitic steel and a nickel-based alloy significantly increased the susceptibility to vanadium pentoxide attack; a cobalt-based alloy (46% Co), on the other hand, exhibited behaviour intermediate between that of nickel- and iron-based alloys free from cobalt.<sup>16</sup> Harris, Child and Kerr<sup>22</sup> found that alloys containing 50–65% Fe, 20% Cr, 12–30% Ni, and up to 18% Co are distinguished by



TABLE VII.—EFFECT OF STILL ATMOSPHERES ON ADDITIVE CORROSION ACCELERATION.<sup>23</sup>

Additive	Metal	Ratio of Additive to Ash	Weight Loss (mg./sq. cm./100 hr.)	
			Air passed	Air not passed
20 Mesh Vermiculite	G.18B	0	143.0	106.0
		1	421.0	181.5
		2	40.5	1.9
		2½	8.3	3.9
Aluminium Oxide	G.18B	0	143.0	106.0
		0.66	100.7	47.8
		1	59.1	38.1
		2	589.0	29.3
	Nimonic 80	0	15.3	19.1
		0.66	9.1	8.3
		1	12.7	6.7
		2	68.7	21.9

exceptionally low resistance to vanadium pentoxide. Intensified study of alloy compositions appears to reveal composition ranges of exceptionally low oxidation resistance, but has not yet produced any pointers to alloys with more favourable characteristics.

A more systematic approach is to select a fairly resistant base metal such as nickel, and then study the effect of different alloy additions individually. At the National Gas Turbine Establishment, it was found<sup>24</sup> that a Ni-4% Be alloy was 40–50% more resistant than a nickel-chromium based creep-resistant alloy. Additions of 4% Be to a nickel-chromium alloy increased its resistance to attack by 30–50%. Molten vanadium pentoxide does not spread uniformly over the surface of the Ni-4% Be alloy, but leaves patches of clean metal, suggesting that the oxide film is partially protective. If vanadium pentoxide is added intermittently, there is an indication that the rate of attack diminishes with time, in contrast to the linear oxidation of nickel-chromium alloys. Nothing is known of the effect of beryllium on the susceptibility to sulphur penetration. The commercial development of a beryllium-containing alloy resistant both to creep and to residual oil ashes is no doubt eagerly awaited.

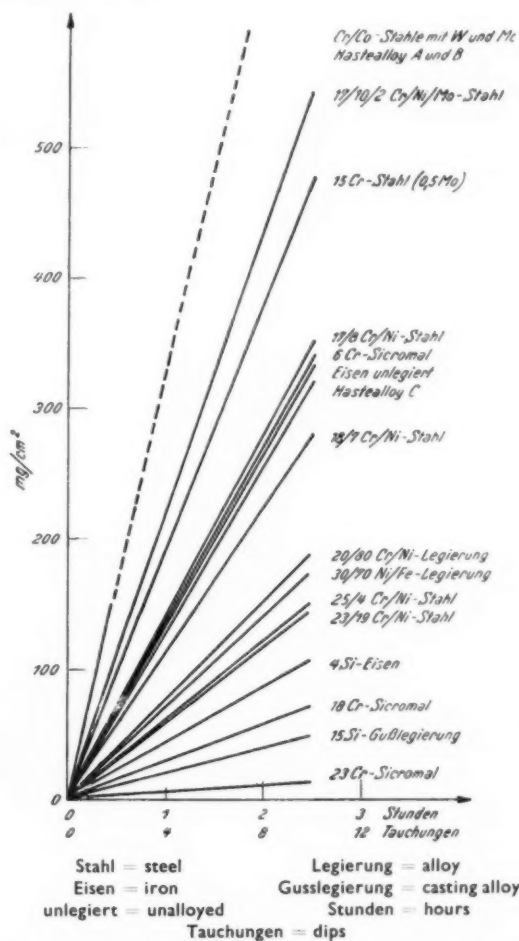
It is at least possible that even higher beryllium contents might be beneficial, but this metal is extremely expensive, and in large concentrations it would be expected to impair the mechanical properties. Under these circumstances, there are obvious advantages in introducing the beryllium as a diffusion coating rather than as an alloying addition.<sup>24</sup> The case for surface treatments is equally strong for other elements, and considerable attention has been paid to the possibility of producing a surface layer of high oxidation resistance on established creep resistant alloys. Electroplating and various gaseous diffusion treatments can produce surface coatings characterised by higher contents of chromium, aluminium or silicon, than can be permitted in the bulk alloys. Alloys containing more than about 25% Cr, and much smaller amounts of the other elements, cannot be forged, are difficult to cast, are brittle, and have poor creep properties.

These considerations are fairly obvious, and their significance has not escaped those who have worked in this field. As long ago as 1949, Leslie and Fontana<sup>25</sup> tried nickel and chromium plating, chromising and aluminising, all without success. Chromium plate is subject to exfoliation,<sup>25</sup> and has been shown to be useless by everyone who has tried it.<sup>10</sup> Chromising is an expensive

TABLE VIII.—REDUCTION OF CORROSIVE ACTION OF ASH MIXTURE WITH MAGNESIA.<sup>25</sup>

Weight Ratio (MgO) Ash	Weight Loss (mg./sq. cm./100 hr.)					
	Air passed			Air not passed		
	G.18B	F.C.B. (T)	Nimonic 80	G.18B	F.C.B. (T)	Nimonic 80
0.25	22.3	7.9	15.3	—	—	—
0.50	0.7	0.5	0.7	—	—	—
0.75	2.7	0.7	0.5	—	—	—
0.80	—	—	—	2.0	0.9	0.7
1.0	0.8	0.7	0.3	—	—	—
1.7	0.9	1.3	0.4	1.5	0.3	0.3
2.0	0.7	0.5	0.5	1.4	0.5	0.3
4.0	2.8	0.6	0.2	0.6	0.6	0.3

process involving the reaction, at high temperatures, of chromium chloride vapour with the metal surface; a chromium-rich surface layer is formed, which interdiffuses with the core alloy. There is a fairly shallow composition gradient between the base and the deposit, and the danger of spalling due to thermal shock is slight. One unsuccessful trial with chromising has already been referred to;<sup>20</sup> it is only fair to report that Evans<sup>7</sup> found some improvement in the oxidation resistance of chromised specimens.

Fig. 36.—Oxidation behaviour of various materials in the presence of vanadium pentoxide, as determined by the rapid sorting test.<sup>10</sup>

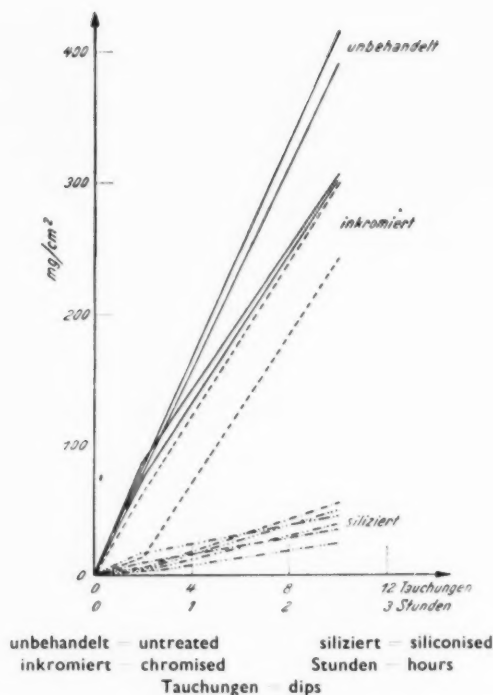


Fig. 37.—Weight loss on specimens of untreated, chromised, and siliconised 18/8 Cr-Ni austenitic steel, after heating at 925° C. in oxygen, with intermittent dips in molten vanadium pentoxide at 900° C.<sup>40</sup>

Attempts at using electrodeposited noble metals were discouraged by the observation<sup>7,23</sup> that even solid platinum is not absolutely resistant to vanadium pentoxide attack.

Other methods of deposition are hot-dip aluminising followed by a diffusion treatment, and "metallising" with a spray pistol. Aluminium impregnation of boiler and heat exchanger tubes has given quite promising results in American trials; beneficial effects are also reported for sprayed coatings of an Fe-26% Cr alloy.<sup>28</sup>

Little is known about the effects of silicon. Of the refractories, silica appears to have the best resistance to fluxing by vanadium pentoxide; Lucas, Weddle, and Preece<sup>23</sup> used silica plates in their experiments with Seger cones made of various mixtures of vanadium pentoxide and other oxides, and were surprised to find that they suffered no attack at all. The formation of a protective scale rich in silica required a high silicon content in the surface layers. For reasons already mentioned, this can only be achieved by means of a surface treatment. A variety of such treatments have been devised; packing components in crushed silicon or ferro-silicon<sup>36</sup> and soaking for a long time at a high temperature; a similar diffusion treatment with a volatile chloride as a carrier;<sup>37</sup> and electrolysis in molten sodium silicate.<sup>38</sup> It is also possible, by the use of mixtures of volatile chlorides, to produce diffusion layers containing other elements, such as aluminium or titanium, as well as silicon, and to suppress the formation of brittle silicides.<sup>39</sup> Such layers can be formed on austenitic steels, provided the nickel content is not too high, and it is claimed that they do not spall due to

thermal shock<sup>39</sup> and are extremely resistant to catastrophic oxidation.<sup>40</sup>

The beneficial effect of silicon is attributed to the acid behaviour of silica in the presence of molten oxides. Comparative tests were carried out on 18/8 austenitic stainless steel, untreated, chromised and siliconised. The specimens were exposed to a slow current of oxygen in a tube furnace at 925° C.; every quarter of an hour they were dipped in molten vanadium pentoxide at 900° C. The results, illustrated Fig. 37 show that the specimens with the silicon-rich surface layer were much more resistant to attack than the others, although even chromising produced some improvement over the untreated steel.<sup>40</sup> Specimens of a 15% Cr steel, after 5 hours at 925° C. with intermediate dips in vanadium pentoxide, are shown in Fig. 38. The untreated steel on the left has been severely attacked, the chromised steel in the middle appears to have a somewhat more resistant surface layer, while the siliconised specimen on the right appears to have suffered no attack at all. Similar effects are shown in Fig. 39 for a 25/20 Cr-Ni steel. Short wires, 2 mm. in diameter, were exposed to the same sorting test as the previous specimens for 5 hours. The untreated wire, at the top of the photograph, shows considerable thinning, the chromised wire shows breakdown of the surface layer accompanied by severe attack below it, while two wires with increasing silicon contents in the surface zones are substantially free from attack. It is unfortunate that this siliconising treatment cannot be applied to nickel-based alloys,<sup>39</sup> which tend to be used in the most sensitive applications because their creep properties are superior to those of the austenitic steels.

Other experimenters obtained less encouraging results in tests with experimental nickel alloys containing up to 15% Si.<sup>16</sup> Small sheet specimens were exposed for 284 hours at 850° C. with 10 mg. V<sub>2</sub>O<sub>5</sub>. The results are given in Table IX, from which it will be seen that although the silicon-rich alloys are the best, they are not significantly better than other nickel-based alloys.

The dramatic advantages claimed by Fitzer and Schwab for their siliconising treatment<sup>39, 40</sup> need to be confirmed by reliable tests, but it is possible that for some applications their treatment may be of practical value.

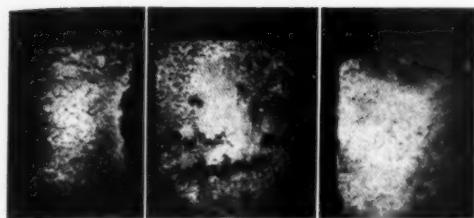
## Conclusions

Various aspects of the problem of vanadium pentoxide in residual fuel ash have been considered at what some readers may by now regard as inordinate length, and a reasonably balanced view of the present position can be derived from the facts which have been presented.

TABLE IX.—WEIGHT-LOSS OF SPECIMENS HEATED AT 850° C. FOR 284 HOURS WITH ADDITIONS OF 10 mg. OF V<sub>2</sub>O<sub>5</sub> EVERY 24 HOURS.<sup>16</sup>

Material	Weight Loss (mg.)	Weight Loss without V <sub>2</sub> O <sub>5</sub> (mg.)	Weight Loss due to V <sub>2</sub> O <sub>5</sub> (mg.)
18 Cr, 8 Ni, 3 Mo Steel . . . . .	1,674	54 <sup>a</sup>	1,620
25 Cr, 20 Ni Steel . . . . .	1,494	60 <sup>a</sup>	1,434
18 Cr, 8 Ni Steel . . . . .	1,325	27 <sup>a</sup>	1,298
37 Ni, 18 Cr, 2 Si Steel . . . . .	1,054	40 <sup>a</sup>	1,014
Nickel . . . . .	582	880 <sup>a</sup>	Nil
20 Cr, 4 Al, Nickel . . . . .	280	18 <sup>a</sup>	262
80 Ni, 20 Cr . . . . .	194	24 <sup>a</sup>	170
20 Cr, 21 Ti, Nickel . . . . .	290	88	202
20 Cr, 20 Co, 21 Ti, Nickel . . . . .	256	61 <sup>a</sup>	175
80 Ni, 14 Cr, 6 Fe . . . . .	186	15 <sup>a</sup>	171
10 Si, 3 Cu, Nickel . . . . .	435	416	19
15 Cr, 5 Si, Nickel . . . . .	165.0	54.8	110.2
14 Cr, 10 Si, Nickel . . . . .	151.5	19.5	132.0
15 Cr, 15 Si, Nickel . . . . .	208.1	65.1	143.0

<sup>a</sup> Taken in proportion to time of treatment from other tests. Test discontinued after 168 hr.



(a) (b) (c)

Fig. 38.—Specimens of 15% Cr steel after 5 hours at 925°C. with intermittent dips in molten vanadium pentoxide: (a) untreated; (b) chromized; (c) silicized.<sup>10</sup>

Large gas turbines for power generation or marine transport can operate at temperatures above 600°–650°C. with relatively expensive fuels, or below that temperature level with residual oil. Major economies can be achieved by burning powdered coal and, in some areas, peat, and experiments with this aim are proceeding. Great economic advantages could be gained by the use of residual oils in turbines operating at higher temperatures; some difficulties which stand in the way of this objective have been discussed and possible methods of overcoming them reviewed.

When the gas turbine builders first publicised the trouble they were having with vanadium pentoxide in residual oils, there was quite a little research boom. The suppliers of various high temperature alloys tried out the effects of vanadium pentoxide on their own products; small firms operating obscure surface treatments had visions of an enormous market opening before them; the gas turbine builders themselves, and for all I know even the oil companies, tried to find various additives. As a result of this research effort, a large body of empirical information about the effects of vanadium pentoxide has been built up, and considerable progress has been made in understanding the mechanism of catastrophic and accelerated oxidation. But no easy practical solution has been found; further systematic research is required before the few experimental results which point the way to the development of promising alloys or surface treatments have been confirmed, fully evaluated and developed. It is not enough to find an alloy which resists oxidation and sulphur penetration stimulated by vanadium pentoxide and chlorides, the alloy must also have all the properties of the materials at present in use. It must have good creep and high-temperature fatigue resistance; it must be resistant to mechanical and thermal shock; it must be made of materials available in substantial quantities; it must lend itself to the methods of production which will form it into turbine components; and it must not be too expensive. Similar demands will be made in the case of surface treatments, although in this case less material is used, so that availability and cost are not so critical, and the process can probably be applied last, so that the effect on manufacturing is less important. Some new problems will arise, however; the difference in chemical composition between the surface layers and the core will be accompanied by differences in thermal expansion characteristics which may have a profoundly detrimental effect on the resistance to thermal shock; a brittle surface layer may cause the whole component to behave in a brittle manner, while a soft surface layer may lower the fatigue resistance of the

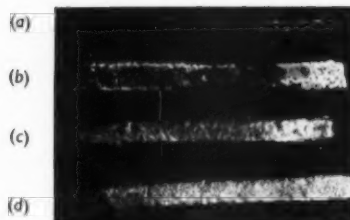


Fig. 39.—Specimens of 25/20 Cr-Ni steel wire after 5 hours at 925°C. with intermittent dips in molten vanadium pentoxide: (a) untreated; (b) chromized; (c) and (d) with increasing silicon contents at the surface.<sup>10</sup>

whole component. The difficulties to be overcome are formidable; but human ingenuity has dealt with other problems, and there is no reason to believe that it has become exhausted.

### Acknowledgments

In an article of this type, the majority of the illustrations are reproduced from earlier work, and in all cases where they are not the author's own work, the appropriate reference number is included in the caption. To the authors and publishers concerned, grateful acknowledgment is made. Special thanks are due to Mr. J. B. Bucher, Blackburn & General Aircraft, Ltd.; Mr. J. Campbell Murray, of John Brown & Co. (Clydebank), Ltd.; Mr. H. Lewis, of the Mond Nickel Research Laboratory; Mr. S. H. Frederick, of the Parsons and Marine Engineering Turbine Research and Development Association; Mr. R. G. Voysey, Chief Scientists' Division, Ministry of Power; Mr. T. Robinson, of C. A. Parsons & Co., Ltd.; Mr. H. F. Cleere, of the Iron and Steel Institute; Mr. R. W. Reynolds-Davies, of the Institute of Fuel; and Mr. B. G. Robbins, of the Institution of Mechanical Engineers; who were particularly helpful in providing original photographs and blocks.

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## Argonarc Welding on Sports Car Bodies

**I**N the fabrication of the body shell of the Austin Healey sports car by Jensen Motors, Ltd., of West Bromwich, the Argonarc process is being employed for the welding of all panel joints.

In view of the necessity for stability at high speeds, the chassis is a fabricated steel structure of considerable depth, and additional strength is provided by the body side panels, which are also of steel. The remainder of the shell, comprising the front and rear ends and the top decking, are of 16 s.w.g. aluminium-manganese alloy, B.S.1470 NS3. The combination of materials affords considerable strength and results in a favourable overall strength-weight ratio.

In the complete car, the alloy structure consists of two large dimension one-piece sections, covering the whole of the upper surfaces before and behind the cockpit, respectively. In order to simplify both assembly and tooling, each of the main panels is built up from a number of smaller sections which are welded together. This assembly method results in a reduction of both the size and complexity of formed parts, the majority of which are given their basic shape in a rubber-platen press.

The method of forming re-entrants, flanges and small cut-outs is hand panel-beating carried out in special jigs. Accuracy and perfection of finish on assembly is essential,

and accurate jiggling and a high welding standard are required to render the panel joints invisible.

The Argonarc process affords protection from oxidation, enables welding to be carried out with speed, and only minimum distortion results from the cooling effect of the shroud of argon gas.

The jigs which clamp the panels firmly in alignment have been designed to maintain correct spacing between joint faces, and also to control the underbead. The jig used for the nose assembly is provided with clamps which are specially shaped to form accurate welding guides. They automatically position the panels so that a weld gap of about  $\frac{1}{16}$  in. is provided. For the bonnet top assembly, the upper half of the clamp is slotted along the centre line to give access of about  $\frac{1}{4}$  in. on each side of the joint line. To provide easy access with the welding torch, the sides of the slot so formed are chamfered.

The degree of penetration is controlled by a semi-circular groove on the lower fixed half of each clamp, which provides a neat underbead which is  $\frac{3}{16}$  in. wide and  $\frac{1}{8}$  in. deep. All proud metal on the outer visible surface is ground away to provide a smooth finish, and the underbead forms a reinforcement to the joint, therefore. Post-weld treatment is not required.

Before the completed nose section is mated to the bonnet top panels, the upper rear edges are trimmed to the required angle by guillotines which provide a clean and accurate face necessary for welding. The nose section is then welded to the upper panels in another jig and the fabrication of the large front panel is then completed.

Each pair of torches is supplied with current from a Quasi-Arc ACP 2/300 transformer set, which is capable of supplying 300 A. to each torch simultaneously. To provide immediate re-ignition of the arc at the zero point in each half cycle, and to ensure automatic initial ignition without contact between the electrode and the work-piece, high-frequency units are inserted in each circuit. Also included in the circuit is a B.O.C. D.C. suppressor unit.

Mk. III water-cooled torches are used and the flow of argon and water is controlled by an economiser unit. Open-circuit voltage is 100 V., each torch taking 127 A. The average welding speed is approximately 10 in./min. Argon is fed at the rate of 12-16 cu. ft./hr., and consumption of this gas is little more than 2 cu. ft. per body.

### Change of Address

THE Induction Heating Department of British Geoc Engineering Co., Ltd., has moved to new premises at Station Road, Edenbridge, Kent, which provide facilities for the expansion of the Department's work on ferrous and non-ferrous billet and tube reheating furnaces for use in connection with such hot working operations as rolling, forging and extruding.



The upper rear edges of the nose sub-assembly are cut to the correct angle in this guillotine.



# Metallurgical Defects in High Speed Steels

By E. Niesielski, L.I.M.

*Following a brief reference of the requirements of a cutting tool, and of the control necessary to ensure their being met, the author describes the various defects—apart from common defects such as piping, non-metallic inclusions, etc.—which arise in high speed steels during steel-making, heat-treatment and tool processing.*

DESPITE the development and constant improvement of sintered carbides, a large number of present-day tools are made from high speed steel. Sintered carbides, being very hard, are also exceedingly brittle, and where heavy vibration and a certain degree of bending are unavoidable during the machining operations, sintered carbide tools will tend to snap, whereas high speed steel tools will successfully stand up to the working conditions, due to their greater toughness.

The consumption of high speed steel in Great Britain in 1955 was about 10,200 tons. Taking an average price of £1,000 per ton, the total value of this steel used in this country in that year amounted, in round figures, to £10 million. As the market value of the tools made from high speed steel is probably more than three to four times the value of the steel utilised for their manufacture, the amount of money involved in tools alone is considerable.

Due to the shortage of tungsten during the last World War, tungsten-molybdenum, molybdenum-tungsten and molybdenum high speed steels were widely introduced. In 1942, the Ministry of Supply issued an order according to which licences were given almost exclusively for high speed steels containing not more than 6½% tungsten. These low tungsten high speed steels, in which part of the tungsten was replaced by molybdenum and/or vanadium, unfortunately became known commercially as "substitute high speed steels." Respectable tool steel makers were shaking their heads, regretfully admitting these steels into their catalogues. As the word "substitute" has acquired a suggestion of inferiority, high speed steels containing molybdenum were not considered equal to tungsten grades. This prejudice was, to a certain extent, based on the fact that high speed steels containing molybdenum are more prone to decarburisation than tungsten-bearing steels. Yet, when properly treated—as they should be—high speed steels of this type are at least equal in cutting performance to tungsten grades.

Table I gives production figures for high speed steels

TABLE I.—PRODUCTION OF HIGH SPEED STEELS IN 1955.\*

Type of Steel	Great Britain		U.S.A.	
	Tons	%	Tons (short)	%
<b>Molybdenum Grades</b>				
No. W % Mo % Cr % V %				
1 6 5 4 2	—	—	10,500	42.00
2 2 9 4 1	—	—	5,900	23.60
3 9 4 2	—	—	4,100	16.40
4 Super high speed steel (molybdenum grade)	—	—	1,100	4.40
Total molybdenum grades	—	18.00	21,600	86.40
<b>Tungsten Grades</b>				
No. W % Cr % V %				
1 18 4 1	—	—	2,400	9.60
2 18 4 2	—	—	300	1.20
3 Super high speed steel (tungsten grade)	—	—	700	2.80
Total Tungsten Grades	—	82.00	3,400	13.60
Total High Speed Steel	10,200	100.00	25,000	100.00

\* Figures for U.S.A. were taken from the Annual Report of the American Iron and Steel Institute for 1955. The total figure for high speed steels produced in Great Britain was taken from the Statistical Yearbook for 1955 of the British Iron and Steel Federation. The percentage figures of high speed steels produced in Britain was obtained through the courtesy of the High Speed Steel Association. These were given as "the sales of high speed steel made by Members of the Association." Although it may not be correct to assume them as the production figures for the whole country, they should not be far from accurate.

made in Great Britain and the U.S.A. for the year 1955, and indicates the opposite trends in the type of high speed steel used in this country and the U.S.A. While the American practice favours tungsten-molybdenum, molybdenum-tungsten and molybdenum grades, British practice relies mainly on the tungsten types. The criterion for using a particular type of steel is its suitability for the purpose required, preference being given for the steel with the lowest cost. In the case of high speed steels used for the manufacture of cutting tools, the requirement is a satisfactory cutting ability at an economical price.

Table II, taken from "A Special American Machinist Report—How to Work Tool and Die Steels," published in *American Machinist* of October 16th, 1950, gives metallurgical properties, among others, of various types of high speed steels. This Table indicates the superiority in mechanical properties and cutting ability of 6/5/4/2

TABLE II.—APPROXIMATE METALLURGICAL CHARACTERISTICS FOR SELECTING TOOL STEELS.\*

Type of Steel	Cutting Ability	Wear Resistance	Red Hardness	Toughness	Hardness (R <sub>c</sub> )	Resistance to Decarburisation	Safety in Hardening
<b>Molybdenum Grades</b>							
W % Mo % Cr % V % Co %							
6 5 4 2 —	68	78	76	35	63-67	Poor	Fair
2 9 4 1 —	68	78	72	35	63-65	Poor	Fair
6 5 4 2 8	96	88	91	17	64-66	Poor	Fair
<b>Tungsten Grades</b>							
W % Cr % V % Co %							
18 4 1 —	63	75	72	25	62-65	Good	Good
18 4 2 —	78	87	75	15	63-65	Good	Good
18 4 1 5	76	77	88	10	64-66	Poor	Fair

\* High numbers represent better characteristics.

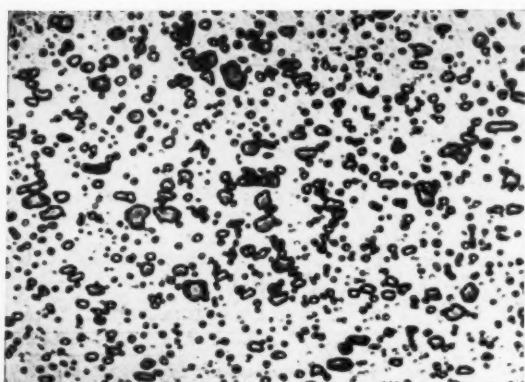


Fig. 1.—Annealed 6/5/4/2 steel. Hardness—V.P.N. 255, R<sub>c</sub>23.  $\times 800$

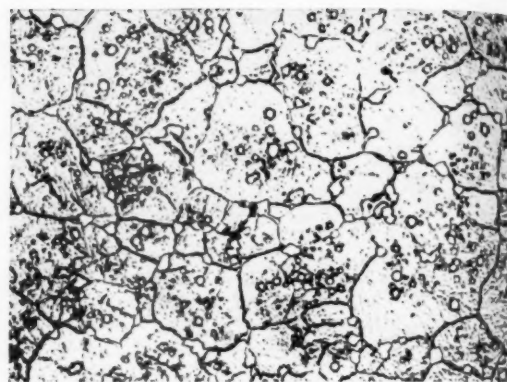


Fig. 2.—Hardened 2/9/4/2 steel. Hardness—V.P.N. 840, R<sub>c</sub>65.  $\times 750$

and 2/9/4/1 molybdenum-tungsten high speed steels over 18/4/1 tungsten high speed steel.

Another factor must be taken into consideration, namely, specific gravity. Table III gives the specific gravities of some of the high speed steels, and also indicates the percentage difference in weight in relation to 18/4/1 steel. It will be seen that a smaller weight of steel is required to produce exactly the same tool from molybdenum-tungsten than from straight tungsten grades of high speed steel.

TABLE III.—SPECIFIC GRAVITIES OF HIGH SPEED STEELS.

Type of Steel				Specific Gravity (g./cc.)	Relative Weight	Weight of 10 ft. of $\frac{1}{2}$ in. Diameter Bar (lb.)
W %	Mo %	Cr %	V %			
18	—	4	1	8.68	100.0	7.404
6	9	4	2	8.15	93.9	6.948
2	9	4	1	8.00	92.2	6.826
—	9	4	2	7.88	90.9	6.730

The above mentioned factors, namely superior mechanical properties, lower specific gravity, and the fact that tungsten-molybdenum steels are less expensive by approximately 10.5% (July, 1957) than tungsten-bearing qualities, would favour the use of tungsten-molybdenum over straight tungsten grades of high speed steel.

In order to achieve low manufacturing costs, long production runs of tools are required. A well-designed tool, made from the most suitable material and metallurgically in its best condition, makes these runs possible, and is, therefore, one of the factors contributing to increased productivity.

Apart from the design, the following metallurgical factors govern the quality of a tool :—

- (1) Material used for its manufacture (the following properties are involved : "red" hardness, wear resistance and toughness).
- (2) Heat-treatment.
- (3) Processing received either before or after heat-treatment (welding, grinding, etc.).
- (4) Surface treatments (nitriding, chromium plating, steam tempering, etc.).

To ensure the production of a good tool, metallurgical control of its manufacture is necessary. The purpose of this is (a) prevention of defective or unsuitable material

going forward into production ; (b) determination and control of heat-treatment ; (c) control of grinding operations with a view to preventing their effects from causing damage to the tools ; (d) control of welding operations with a view to obtaining a sound weld ; and (e) prevention, location and elimination of various causes of troubles during the manufacture of tools, due to metallurgical or chemical factors. The ultimate aim behind all these controls is the production of tools of high metallurgical quality.

For the best assessment of the quality of high speed steel, the author considers that it should be examined for structure and hardness in the condition in which the tools are to be used, i.e. in the fully heat-treated state. Examination of steel in the annealed condition may not reveal sufficiently the extent of the defects that are apparent in the fully heat-treated state.

The performance test is, of course, the final criterion by which the quality of a tool is judged. Yet it must be borne in mind that the metallurgical condition of the tool is only one of the factors affecting its performance. The design, machining conditions (speed, feed, depth of cut), material being machined, condition of the machine tool, etc., must also be taken into consideration.

The author holds the view that as long as the tool possesses sufficient toughness for the job, the higher its

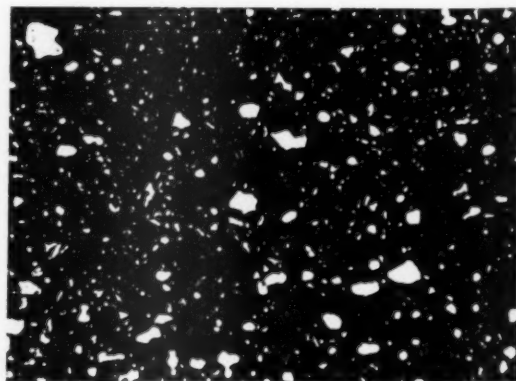


Fig. 3.—Heat-treated 18/4/1 steel. Hardness—V.P.N. 863, R<sub>c</sub>66.  $\times 750$

hardness the better the tool. Therefore, the heat-treatment of the tool should be such as to obtain this optimum condition. Below are enumerated some of the metallurgical defects (common defects such as pipe, non-metallic inclusions, etc., are not included) which can be found in tools made from high speed steels, mainly 18 4/1 (18% W, 4% Cr, 1% V) and 6/5 4/2 (6% W, 5% Mo, 4% Cr, 2% V) types. These defects are not confined to these two types of steel, but can be met in practically all tool steels. They can be classified, broadly, into three groups, namely:—

- (a) Defects arising during the manufacture of the steel.
- (b) Defects arising during the heat-treatment of the tools.
- (c) Defects arising during the processing of the tools.

For the purpose of comparison, before reviewing typical defects, the structure and hardness of the most popular types of high speed steel in the annealed, hardened and fully heat-treated (hardened and tem-

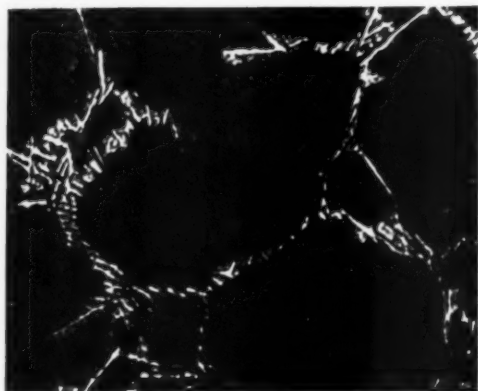


Fig. 4.—Cast 6/5/4/2 steel in the fully heat-treated condition.  $\times 250$

pered twice at 565°C.) conditions are presented in Figs. 1-3. The structure of an ideal high speed steel, in the fully heat-treated condition, should show numerous carbides uniformly distributed in a fully tempered martensitic groundmass.

## STEEL MANUFACTURING DEFECTS

### Insufficient Hot-Working and Carbide Segregation

High speed steel, having a very high percentage of carbide-forming elements, exhibits in the cast condition—apart from the defects peculiar to this state—heavy carbide segregation. This segregation is a result of the formation of a eutectic of austenite and carbides on the solidification of steel. Fig. 4 represents a section taken from the centre of a 4½ in. square ingot in the fully heat-treated condition, showing the presence of eutectic carbides in the continuous form in the grain boundaries.

The breakdown of this original structure is one of the objects of hot-working operations. The heating for these operations assists, by a process of diffusion, in producing homogeneity of the steel. The highest possible reduction of area from ingot to billet by hammer cogging results in the best carbide distribution. Fig. 5

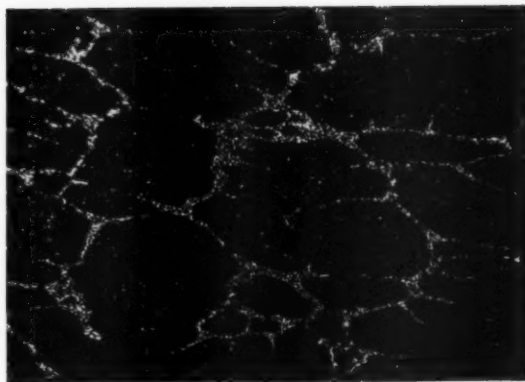


Fig. 5.—Insufficiently hot-worked 6/5/4/2 steel in the fully heat-treated condition.  $\times 140$

may serve as an example of an insufficiently hot-worked steel. The carbides are still in the form of envelopes located in the areas that originally were grain boundaries.

The defect represented by this photomicrograph can readily be recognised on a fracture test in the fully heat-treated and even annealed conditions. For this purpose, the fracture test should be carried out along the direction of hot-working of the bar. A steel that has received sufficient hot-work exhibits, in the fully heat-treated state, a fine fracture, whereas one that has been insufficiently hot-worked shows a coarse and faceted fracture. Fig 6 illustrates these two conditions. A high speed steel having part of its carbides in the form of envelopes is unacceptable for the manufacture of tools due to excessive brittleness.

Another result of insufficient hot-working by hammer cogging is the presence of areas of carbide segregation and carbide stringers. It should be pointed out, however, that the extent of carbide segregation areas in the high speed steel product depends very much on the degree of the initial distribution of carbides. The latter is governed by a number of factors such as ingot-mould design, pouring temperature, rate of pouring, rate of solidification, etc. If the initial segregation of carbides is not favourable, the segregates can be broken up only with great difficulty by the application of a very extensive hot work.

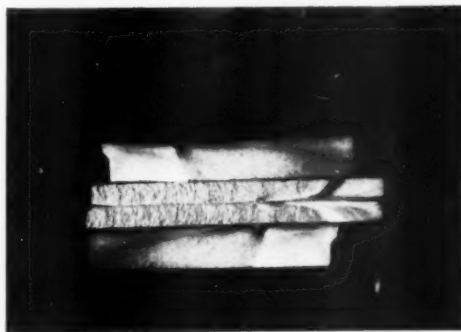
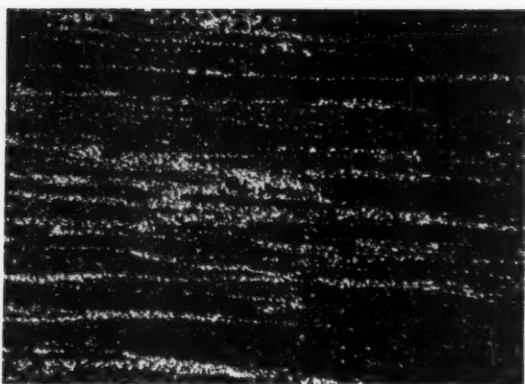


Fig. 6.—Fracture surfaces of coarse and fine 6/5/4/2 steels in the fully heat-treated condition.  $\times 2$



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Fig. 7.—Areas of carbide segregation and stringers in fully heat-treated 6/5/4/2 steel.  $\times 140$

Fig. 7 shows a longitudinal section of a 6/5/4/2 high speed steel with excessive carbide segregation and carbide stringers. Acicular martensite present in these segregated areas, as illustrated by Fig. 8, is characteristic of high hardening temperatures. In this case, "high hardening temperature" applies only to the segregated area. A steel with these defects exhibits, in the fully heat-treated state, a dry, woody fracture when broken longitudinally.

Areas of carbide segregation and stringers, if not joined together and not excessive in size, are not necessarily detrimental to the quality of high speed steel. The objections to a steel that has been insufficiently hot-worked are as follows:—

- (a) After normal full heat-treatment, the areas with heavy carbide segregation may contain a high proportion of untempered (secondary) martensite formed during the last secondary hardening. This martensite, being a very brittle constituent, may be one of the causes of the formation of cracks and/or stresses in grinding, and will, generally, reduce the toughness of the steel.
- (b) The presence of areas of excessive carbide segregation and of untempered martensite may cause snapping of the tool edges.

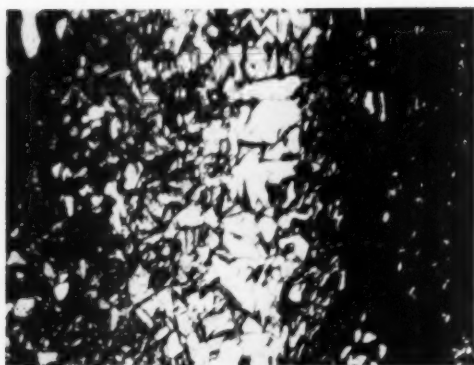


Fig. 8.—Carbide segregation in fully heat-treated 6/5/4/2 steel.  $\times 400$

- (c) Due to the high carbon content in the carbide segregated areas, carbides containing high percentages of carbon may form or be already present. Depending on the austenitizing temperature applied during the hardening treatment, some of them may become liquid. On cooling, this liquid phase will solidify in the form of carbides in the grain boundaries, resulting in a structure illustrated in Fig. 26.
- (d) The welding of high speed steel containing carbide segregation results in the production of areas of a burnt, eutectic, structure. These areas, apart from reducing the toughness of the steel, are detrimental to machinability, due to their relatively high hardness—up to V.P.N. 380 after full annealing. Fig. 27 illustrates this defect.
- (e) Regions of excessive carbide segregation may form planes of weakness and, as such, are stress raisers.
- (f) A high speed steel in which carbide segregation is insufficiently broken down is more brittle than one with random distribution of carbides.
- (g) Porosity or internal forging bursts are usually associated with excessive carbide segregation.

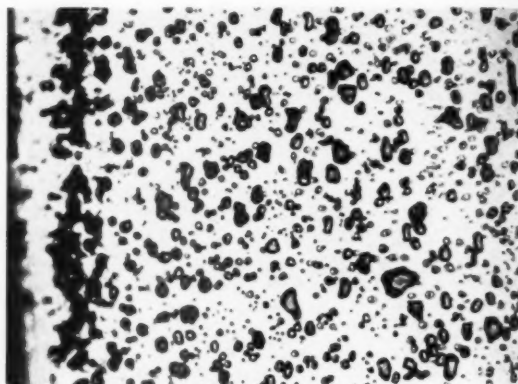


Fig. 9.—Layer of scale on annealed 18/4/1 steel  $\times 800$

### Large Carbides

The majority of carbides in high speed steels in the annealed condition should be well under 0.0001 in.  $\times$  0.0001 in. when examined microscopically. A certain proportion of carbides, measuring up to 0.0002 in.  $\times$  0.0003 in., is usually present in these steels. Large carbides, and especially those measuring 0.0005 in.  $\times$  0.001 in.  $\times$  0.0005–0.001 in., are detrimental for two reasons: (a) they cause difficulty in machining; (b) they cause difficulty in hardening.

Table IV, taken from "Grindability of Tool Steels" by L. P. Tarasov, gives the hardness of some of the carbides found in tool steels. For comparison, the hardness of the abrasive compounds used for grinding has also been included. High speed steels containing carbide segregations, which include a considerable proportion of large carbides, are almost impossible to drill, and are difficult to saw and mill, although their hardness is only V.P.N. 250–280 (R. 23–27). The steels with a high vanadium content are difficult to machine,



due to the high hardness of vanadium carbide. This class of high speed steel presents a special problem during final grinding after the full heat-treatment, as a greater proportion of vanadium carbide (VC) remains undissolved than of the tungsten-molybdenum-rich carbides,  $\text{Fe}_4\text{W}_2\text{C}$  or  $\text{Fe}_3\text{Mo}_2\text{C}$  (all chromium carbides go into solution.)

When fully heat treated under standard conditions, high speed steels with a considerable proportion of large carbides develop low hardness. This is due to the small surface area of the carbides in relation to their volume, resulting in sluggishness in dissolving in the matrix of the steel. The fracture appearance of such steels is similar to the high speed steels exhibiting "fish scale."

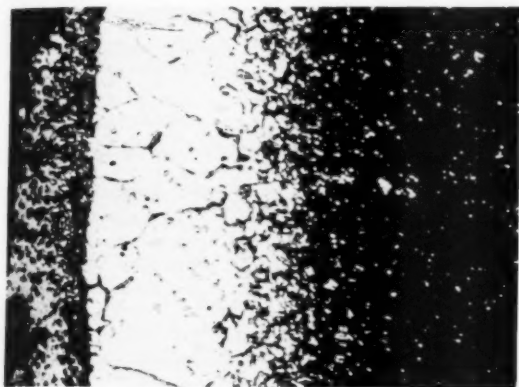
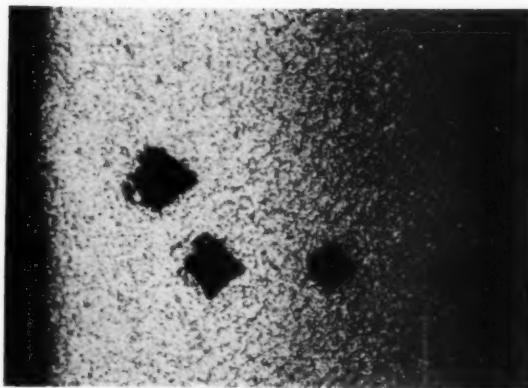


Fig. 10.—Fully heat-treated 18/4/1 steel decarburised at the surface.  $\times 260$

#### Presence of Scale

This defect may appear unimportant, yet under certain conditions it will produce extremely harmful results. High speed steel wire for the manufacture of small tools is sometimes used in a drawn state, with a manufacturing tolerance of several thousandths of an inch per side. Occasionally the wire may be supplied with a very thin layer of iron oxide, as shown in Fig. 9, which represents a longitudinal section of an annealed 18/4/1 high speed steel with a layer of scale up to 0.002 in. thick. Fig. 10 shows the structure at the surface of the same specimen after full heat-treatment! The steel has been decarburised on the sides up to a depth of 0.006-0.008 in., whereas it shows carburisation up to 0.002 in. on the cut surface.

This test piece of high speed steel was hardened in a gas-fired semi-muffle furnace with a reducing flame forming a protective curtain at the entrance to the furnace. It would appear that under these conditions the oxygen in the scale reacted with the carbon in the steel, resulting in the formation of a deep ferritic layer in the steel. Test pieces from which the scale had been removed, and which had been hardened at the same



Distance from the Surface (in.)	Hardness	
	V.P.N.	R <sub>c</sub>
0.012	575	54
0.024	701	60
0.030	766	63
0.035	810	64

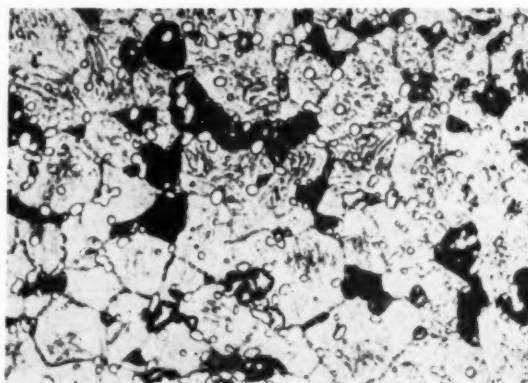
Fig. 11.—Fully heat-treated 6/5/4/2 steel decarburised at the surface.

time, showed carburisation up to 0.002 in. deep, all round.

#### Decarburisation

This defect may either be full or partial (carbon gradient), with varying degrees of the latter. The former can readily be detected on a fracture test or microscopically in the annealed or fully heat-treated conditions. The latter can be fully determined microscopically by hardness test and, to a certain degree, on fracture test, after full heat-treatment. Fig 11 shows a section of a 6/5/4/2 high speed steel,  $\frac{3}{16}$  in. in diameter, in the fully heat-treated condition, which exhibits a decarburised layer up to 0.035 in. deep.

One of the methods of determining the depth of a carbon gradient is to harden a sample of high speed



Distance from the Surface (in.)	Hardness	
	V.P.N.	R <sub>c</sub>
0.004	524	51
0.015	655	58
0.025	766	63
0.032	810	64

Fig. 12.—Decarburised layer in hardened 6/5/4/2 steel.  $\times 800$

TABLE IV.—HARDNESS OF CARBIDES.

Material	Hardness (Knoop H <sub>30</sub> )
Iron Carbide, $\text{Fe}_3\text{C}$ .. .. .	1150
Chromium Carbide, $\text{Cr}_7\text{C}_3$ .. .. .	1820
Vanadium Carbide, VC .. .. .	2520
Aluminium Oxide, $\text{Al}_2\text{O}_3$ .. .. .	2440
Silicon Carbide, SiC .. .. .	3590



Fig. 13.—Annealed 1½ in. diameter bar of 18/4/1 steel containing 10% cobalt. × 8

steel and examine it microscopically. Areas depleted in carbon will contain a proportion of a black etching constituent, bainite. Fig. 12 shows the same steel as that in Fig. 11, but in the hardened condition, with a 0.032 in. deep carbon gradient as indicated by the presence of bainite.

A satisfactory determination of the depth of both full and partial decarburisation in high speed steel in the annealed condition can be made by etching a polished specimen for about 40 seconds in a solution of 4% nitric acid in methyl alcohol.

Visual examination reveals the presence of three zones: the first, which is light etching, is a fully decarburised zone, and is ferritic or nearly so; the second—etching light brown—is a transition zone which is partially decarburised; and the third light blue etching zone is the basis material having full carbon content. Fig. 13 shows an annealed high speed steel, decarburised up to 0.050 in., as indicated by the presence of two zones—fully and partially decarburised—before full carbon content is reached.

#### Carburisation

Final annealing of high speed steel bars or coils is usually carried out in partially sealed containers into which a small quantity of a carbonaceous matter has been added in order to take care of the oxygen present

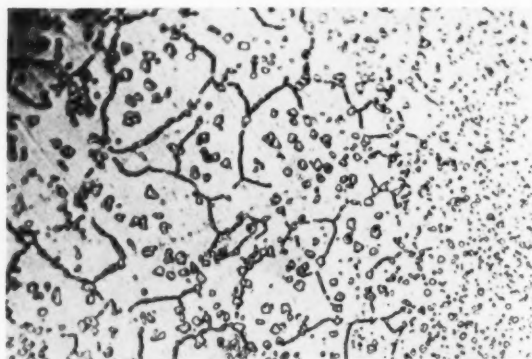
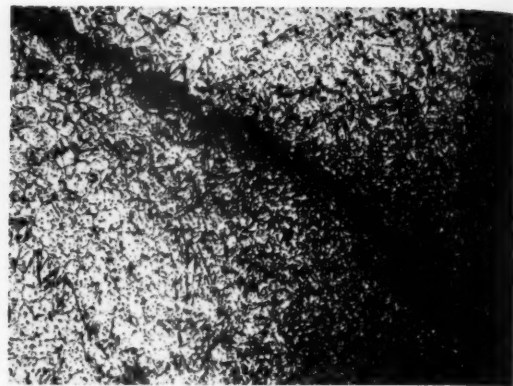


Fig. 15.—Carbide network in an annealed 6/5/4/2 steel. × 800



Distance from the Surface (in.)	Hardness	
	V.P.N.	R <sub>c</sub>
0.014	648	58
0.021	734	62
0.026	835	65
0.045	920	67.5
0.100	890	66.8

Fig. 14.—Fully heat-treated 6/5/4/2 steel carburised at the surface. × 140

in the containers. Fig. 14 is an extreme example of carburisation which had been imparted to the steel during the annealing of bars. The carburised layer has a depth of approximately 0.060 in. The carburised case contains numerous cracks, most of which have developed during the hardening operation: some have formed during the secondary hardening treatments. Outside layers of the case, due to a very high carbon content, exhibit a burnt structure.

Carbon lowers the  $M_s$  point—the temperature at which the formation of martensite commences. As the steel at lower temperatures is less able to accommodate the stresses accompanying this reaction, the formation of internal stresses and the occurrence of hardening cracks are thus promoted. Carbon is also known to lower  $M_f$  point—the temperature at which the formation of martensite from austenite ceases. This favours the retention of austenite on hardening.

Table V shows the hardness of a carburised 6/5/4/2 steel after hardening at 1,220°C., and tempering at 565°C.

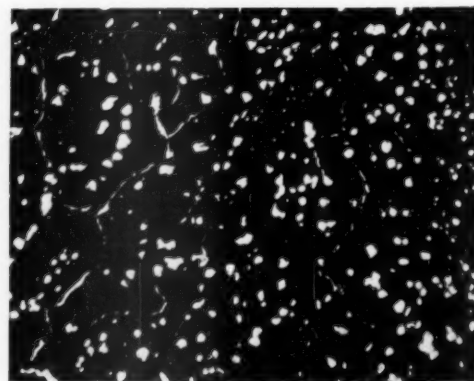
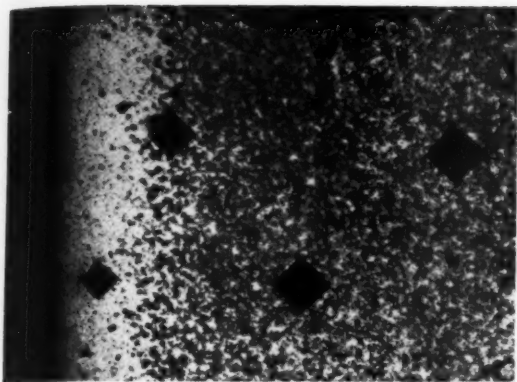


Fig. 16.—Carbide network in a fully heat-treated 6/5/4/2 steel. × 800



Distance from the Surface (in.)	Hardness	
	V.P.N.	R <sub>c</sub>
0.003	575	54
0.006	385	38
0.012	275	26

Fig. 17.—Surface layer containing iron borides on 6/5/4/2 steel.  $\times 140$

The marked increase in hardness of the outer layers after secondary hardening indicates that the amount of retained austenite after hardening increases with the increase in the carbon content of the steel. The subsequent transformation of this retained austenite to martensite during the secondary hardening (tempering) operations is mainly responsible for this increased hardness of the outer layers.

Fig. 15 represents a 6/5/4/2 steel showing what is thought to be an attempt by a steelmaker to reclaim a decarburised steel. The presence of a carbide network in the grain boundaries can be noted. The virtues of this treatment have not, as yet, acquired a generally accepted respectability. The argument against carburisation is that carbides formed during this treatment are not complex ones which impart a property of "red-hardness" to high speed steel, but rather are of the Fe<sub>3</sub>C type. Another objection is that the presence of a carbide network in the grain boundaries in a continuous form will cause difficulties in machining, especially milling; may cause cracking in hardening; and will reduce the toughness of the steel due to the retention of this network, after full heat-treatment, as shown by Fig. 16.

#### Pitted and Hard Surface

A complaint which originated in the Sawing Department led to the discovery of an unusually hard surface, up to V.P.N. 650 (R<sub>c</sub> 58), on a steel in the fully annealed condition. This hardness was confined to the pitted areas of bars only. Micro-examination revealed a patchy layer, up to 0.006 in. deep, which is shown etching white in Fig. 17. This defect, it is thought, is

TABLE V.—HARDNESS OF CARBURISED 6/5/4/2 STEEL AFTER HARDENING AND TEMPERING.

At a Depth of (in.)	Hardness (V.P.N.) after		
	Hardening	Second Tempering	Third Tempering
0.007	429	743	747
0.019	519	752	847
0.033	803	920	946
0.045	847	858	882
0.060	882	847	847
0.080	882	835	847
0.250	870	835	847



Fig. 18.—Forging bursts in 6/5/4/2 steel  $\times 1$

due to the application of borax to billets before heating for rolling in order to prevent decarburisation, especially on 6/5/4/2 steel. When large amounts of sodium borate adhere to the steel, pitting of its surface occurs at elevated temperatures, and as a result of physico-chemical reactions—iron borides are formed. These cause the very high hardness of the steel's surface.

#### Miscellaneous Defects

##### Internal Bursts (see Fig. 18)

These defects can readily be recognised by the bright, shiny appearance they present when fractured. This bright metallic appearance is only retained if the bursts have not been exposed to the oxidising atmosphere of the heat-treatment furnaces. In the latter case, especially when the bursts are small, they can easily be mistaken for streaks of non-metallic inclusions.

Assuming that ingots are brought up to the right forging temperature, and that they are forged within the correct temperature range, the origin of this defect can almost invariably be traced to faulty hot-working, namely, too high an initial reduction. It should, however, be added that the condition of the ingot (due to the design of the ingot mould, pouring temperature, solidification rate, etc.) will constitute a contributory factor to the occurrence of this defect.

Owing to the coarse columnar structure and the presence of segregation, the initial hot working of high speed steel ingots should be light, and should not exceed 10% reduction of area. If this initial reduction is too high, internal rupture of the steel may occur. If these ruptures are small and do not become oxidised, they may close up on subsequent hot working of the ingot or of the billet. However, if they are large, their size will be reduced, but the bursts will be present in the final product. When the surfaces of the bursts become oxidised, they will, of course, never close up. When the structure of the ingot has been sufficiently refined, greater amounts of hot work can be given to the ingot.

Since ultrasonic examination of bar material was introduced by the author's company, a surprisingly large number of high speed steel bars has been found to contain internal bursts which previously were not detected or were classified as streaks of non-metallic inclusions.

##### Metallic Inclusions (on a macroscopic scale)

Fig 19 illustrates a section of an 18/4/1 steel containing an inclusion of a medium carbon steel, several

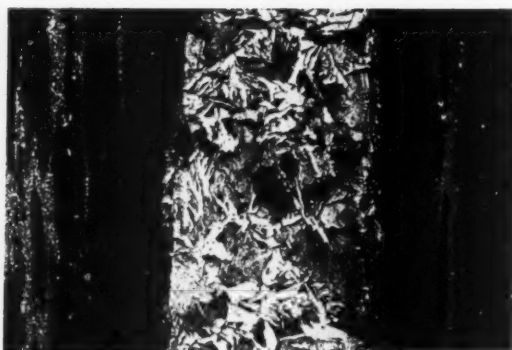


Fig. 19.—Inclusion of medium carbon steel in fully heat-treated 18/4/1 steel.  $\times 150$

inches long. Low carbon steel inclusions a few feet long by a few inches wide by  $\frac{1}{8}$ – $\frac{3}{16}$  in. thick, of low carbon steel, have been encountered. Most of them appear to have been introduced during the hot working operations, but some of them must have been introduced at the teeming stage.

## TOOL HEAT-TREATMENT DEFECTS

### Carburisation

Fig. 20 shows a section of 18/4/1 steel, 0.200 in. diameter, in the fully heat-treated condition, which had been carburised up to 0.004 in. deep during the hardening operation. Due to the increased hardness of the surface layers and the presence of untempered martensite, cutting edges may have a tendency to snip.

### Underhardening

Apart from carburisation, this sample exhibits another defect, namely, underhardening. Its effect is indicated by the low hardness of the steel below the carburised layer. The hardening temperature and/or the holding time applied was too low to obtain sufficient solution of carbides in the matrix of the steel.



Fig. 20.—Fully heat-treated 18/4/1 steel carburised at the surface.  $\times 500$

Case	Location	Hardness	
		V.P.N.	R <sub>c</sub>
...	...	927	67.5
Core	...	780	63

The hardness of a fully martensitic structure depends, predominantly, on its carbon content, the alloying elements having a negligible influence on it. Fig. 21 presents a generally accepted relationship between the carbon content of martensite and its maximum hardness.

Most grades of high speed steel contain by volume, after hardening and tempering, between 8 and 13% of carbides. The two most popular types, 18/4/1 and 6/5/4/2, contain from 8.5–10%. The carbon content of the matrix of these two steels is approximately 0.5%. The remaining 0.2–0.35% is contained in the undissolved carbides.

As hardness is a function of the constituents present, the hardness of these two steels, when properly treated, is usually higher than would be indicated by Fig. 21. V.P.N. 800 (R<sub>c</sub> 64.0), after full heat-treatment, is considered to be the minimum for these two steels when used for the manufacture of cutting tools.

### Undertempering

The purposes of tempering are :—

- The relief of internal stresses set up on hardening during the transformation of austenite to martensite, when expansion occurs.

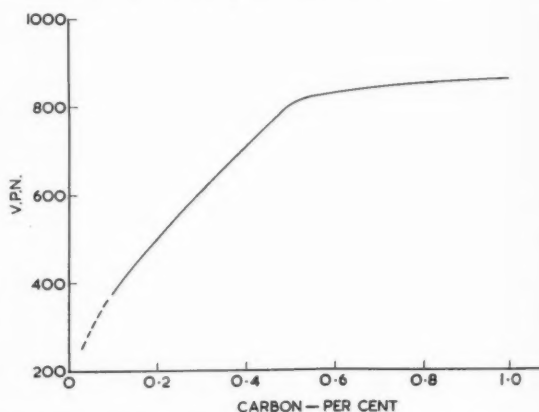


Fig. 21.—Relationship between carbon content of martensite and hardness.

- The change of tetragonal martensite into cubic martensite, which is less brittle.
- The precipitation of complex carbides which contribute to the hardness of high speed steel.
- Secondary hardening: austenite, having been conditioned at the tempering temperature, transforms to martensite (secondary) during the cooling phase of this treatment.\*
- The attainment of dimensional stability. Where high dimensional accuracy is required and is to be retained (gauges, reamers, etc.), transformation of all the austenite is necessary: heating at 565° C. for about 2½ hours will ensure this requirement.

There are two ways in which steel may be under-

\* Since this article was submitted to *Metallurgia* for publication, a paper on "A High Temperature X-Ray Study on High Speed Steels" (*J. Iron and Steel Institute*, May, 1957), has come to the author's notice, in which Dr. H. J. Goldschmidt claims that isothermal transformation of austenite into martensite takes place when hardened high speed steel (18/4/1 type) is heated at temperatures in the range 500°–600° C., which are normal tempering temperatures for high speed steels.



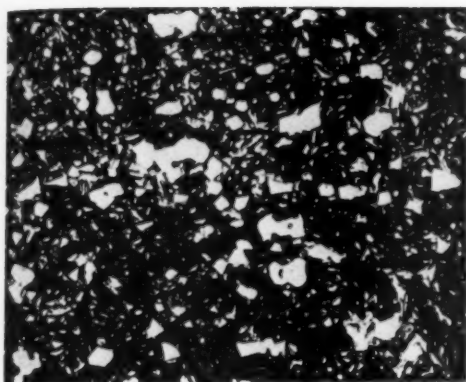


Fig. 22.—18/4/1 steel hardened by quenching in oil and tempering once only at 565° C. Hardness—V.P.N. 870, R. 66.  $\times 750$

tempered. If a hardened high speed steel is heated only once at a suitable temperature (565° C. for 18/4/1 steel) to develop its highest hardness, the martensite formed on hardening has been tempered, but that which was formed during the cooling phase of the tempering operation still remains in the tetragonal form, and the internal stresses set up during its formation are still present. Fig. 22 is a section of 18/4/1 steel in which a secondary (untempered) martensite formed in the tempering (secondary hardening) operation is to be observed. High speed steels that are quenched in oil on hardening and tempered only once to develop full hardness, are particularly prone to show this type of microstructure. Due to a considerable proportion (23–30%) of untempered martensite present in these steels, they possess a high hardness, but their toughness is considerably reduced.

The second way in which undertempering can arise is in the tempering of high speed steel at a temperature below that required to develop its full hardness. Heating hardened high speed steel up to approximately 315° C. results in tempering of primary martensite, but all the retained austenite is left untransformed and the precipitation of complex carbides has not taken place. Hardness, being a function of the constituents present, is therefore low.

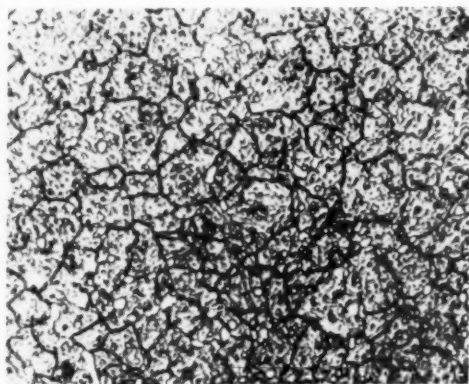


Fig. 23.—6/5/4/2 steel tempered once for 2½ hours at 320° C. Hardness—V.P.N. 762, R. 63; before tempering it was V.P.N. 856.  $\times 600$

Heating hardened high speed steel above 315° C. causes precipitation of complex carbides and conditions the steel for subsequent transformation of austenite to martensite. The effectiveness of this conditioning is a function of temperature and time. Figs. 23 and 24 represent 6/5/4/2 steel tempered for 2½ hours at 320° C. and 500° C., respectively. The existence of austenite in the steel is indicated by the presence of grain boundaries.

A delay in tempering, by holding hardened tools at room temperature, tends to stabilise the austenite and slows down its rate of subsequent transformation to martensite during the secondary hardening operation. It is doubtful, however, whether the magnitude of this retarded transformation is large enough to warrant any special measures to be taken under production conditions.

### Decarburisation

This defect has already been described in the previous section. Whether produced during heating for hot working, annealing or hardening, its symptoms are the same. Mention may be made here of decarburisation which sometimes occurs during heating for hardening in the salt bath. This only happens when a bath is

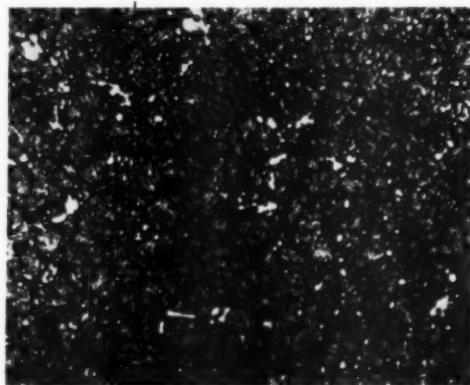


Fig. 24.—6/5/4/2 steel tempered once for 2½ hours at 500° C. Hardness—V.P.N. 810, R. 64; before tempering it was V.P.N. 856.  $\times 600$

contaminated with impurities: the chief culprits are considered to be barium and iron oxides which cause the removal of carbon from the steel. High speed steels containing cobalt are very susceptible to this effect, especially when the time in the high-heat salt bath is long (say 3–4 minutes). A well de-sludged bath is neutral to the steel in this respect.

### Burning

When the hardening temperature exceeds approximately 1,320° C. for 18/4/1 and approximately 1,260° C. for 6/5/4/2 steel, melting of the steel occurs. Fig. 25 shows a section of a fully heat-treated 6/5/4/2 steel which was hardened at the temperature normally used for 18/4/1 steel. The presence of eutectic carbides can be observed.

A high speed steel tool that has been burnt is very prone to grinding hazards and its toughness is considerably reduced, due to its virtually "as cast" structure. Local burning of some of the areas of carbide segregation may occur even though a normal hardening

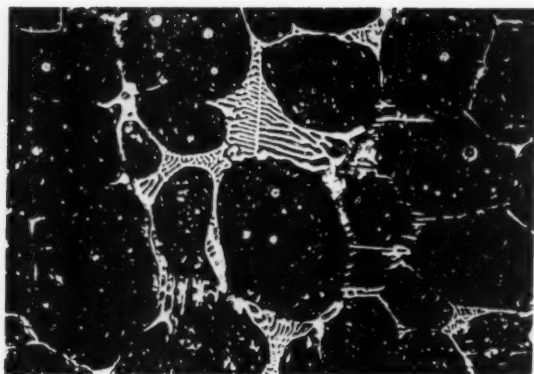


Fig. 25.—Evidence of burning in fully heat-treated 6/5/4/2 steel.  $\times 750$

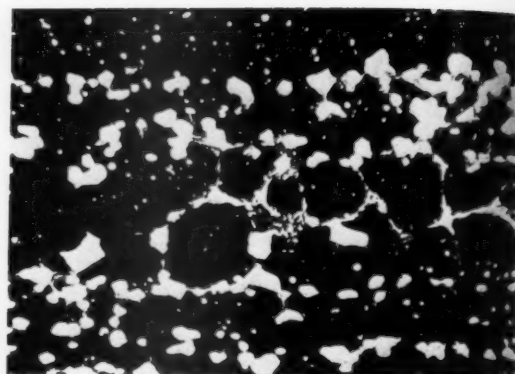


Fig. 26.—Evidence of burning in fully heat-treated 6/5/4/2 steel.  $\times 550$

temperature is used, as has already been mentioned in an earlier section.

#### "Clinking" of Welds During Hardening

In order to economise on high speed steel, the part of a tool which is not intended to cut, i.e. the shank, is made from plain carbon or low-alloy structural steel. The two different portions of a future tool are welded together in an early stage of tool manufacture.

An ideal weld contains practically no eutectic carbides; they should be expelled from it by the upsetting action of the welding machine applied at the final stage of the welding operation. Yet it happens, not infrequently, that the junction of the disturbed zone and the high speed steel proper contains some eutectic carbides. When these are present in a massive form, the ductility of this zone and, therefore, its ability to accommodate stresses due to volume changes (application of heat or a structural transformation) is considerably reduced.

When such tools are hardened in salt baths and the welds are entirely immersed in the high temperature bath, the rapid rate of heating characteristic of this medium causes this disturbed zone to "clink." The "clink" on the surface of the tool will act as a stress-

raiser, resulting in an early failure of a tool. Fig. 27 shows the structure adjacent to a "weld clink" in a welded 18/4/1 high speed steel tool, in a fully heat-treated condition.

#### Cracking

The cracking of high speed steels during heat-treatment can be attributed to a number of causes, including the following:—

- (a) The presence of areas of excessive carbide segregation.
- (b) The presence of a decarburised surface.
- (c) The presence of a seam, crack, etc.
- (d) Ineffective preheating.
- (e) A delay in tempering.
- (f) Inefficient tempering.

Large tools, particularly those of non-uniform design, are susceptible to cracking during heat-treatment. According to J. P. Gill ("Tool Steels"), high speed steel of 18/4/1 composition, when heated for hardening at  $1,290^{\circ}\text{C.}$ , hardens by transformation of austenite to martensite at the temperatures indicated in Table VI. As the  $M_s$  point is a function of both hardening temperature and holding time, the temperatures at which these transformations occur will, therefore, vary. Lower hardening temperatures and/or shorter holding times raise the  $M_s$  point; higher hardening temperatures and/or longer holding times lower it. The extent of carbide solution appears to be the governing factor. Due to the high carbon and alloy contents of areas of carbide segregation, their  $M_s$  point is lowered in relation to that of the general mass of the steel, with the following results:—

- (i) There is a lag in the austenite to martensite transformation, and areas of carbide segregation start to harden when the remainder of the steel is already in a partially-hardened condition.
- (ii) A greater amount of austenite is retained on hardening. On secondary hardening, carbide-segregated areas produce more secondary martensite than the neighbouring areas with normal carbon and alloy contents.

These two factors may produce stresses which can cause fracture, or rather small local fractures, of the

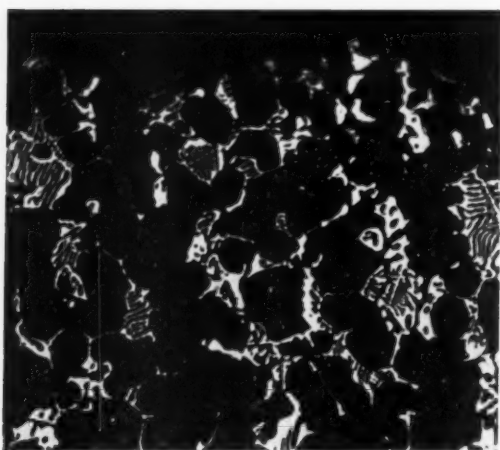


Fig. 27.—Structure adjacent to a "weld-clink" in a welded fully heat-treated 18/4/1 steel tool.  $\times 500$

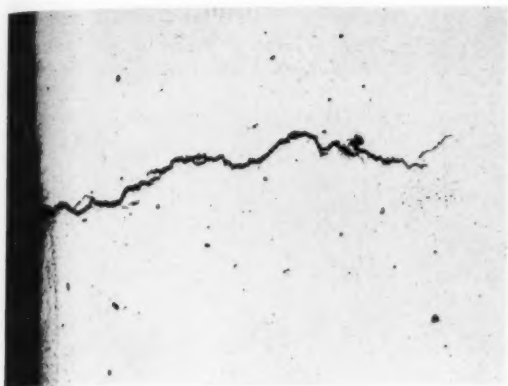


Fig. 28.—Crack in a fully heat-treated 6/5/4/2 steel.  $\times 30$

steel in heavily carbide-segregated areas, either during hardening or secondary hardening operations.

As already mentioned in the section on carbide segregation, due to the high carbon content in the carbide-segregated areas, carbides containing high percentages of carbon may become molten at the hardening temperature. Should this happen, this liquid phase will, on cooling, solidify in the form of carbides which will be deposited in the grain boundaries; Fig. 26 illustrates this defect.

In the subsequent cooling phase of the hardening process, when the actual hardening (austenite to martensite transformation) takes place, expansion of the steel occurs. The presence of the network of high carbon carbides, formed earlier in this operation, restricts the capacity of the steel for movement, with the result that cracks may develop in the areas containing these high carbon carbides.

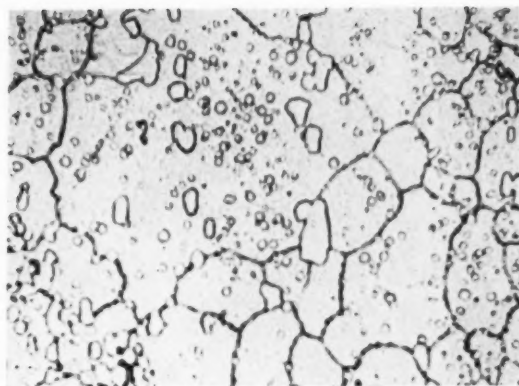
Owing to the difference in timing of the austenite to martensite transformation between the decarburised surface and the remainder of the tool, expansion of the inside of the tool may cause tension in the decarburised layers, which can result in the formation of a crack in these layers on hardening. The presence of a seam, crack, etc., will also cause the propagation of a crack on hardening.

Ineffective preheating before hardening when a salt bath is employed as the heating medium can also lead to cracking. This preheating should take place at a temperature above the  $A_1$  point ( $850^\circ\text{C}$ . is a suitable temperature for both 18/4/1 and 6/5/4/2 steels), and sufficient time should be given for the tool to attain this temperature throughout.

Delay in tempering may also assist crack formation, but although it is advisable to temper high speed steel tools as soon as possible after hardening, a delay of up to one day does not appear to cause cracking in tempering. A low tempering temperature and short holding time at tempering temperature cause the austenite to martensite transformation to take place at low temperatures, and occasional cracking of tools may occur at these temperatures, as high speed steel is less capable of accommodating the stresses accompanying this transformation.

#### "Fish-Scale"

A large grain size, or a mixture of large and small grains, is produced during the hardening of high speed



Reduced  $\frac{1}{2}$  linear in reproduction.

Fig. 29.—Large grains in hardened 6/5/4/2 steel.  $\times 800$

steel, if the hardness of the steel before this treatment is excessive. 18/4/1 steel develops a larger grain size than 6/5/4/2. Mr. J. A. Colley of the Department of Metallurgy, University of Cambridge, has suggested in a private communication that the possible reason for the formation of large grains ("fish-scale") on re-hardening high speed steels is the smaller number of undissolved carbides present in the matrix, due to the initial hardening. During this hardening treatment, about 75% by volume of the carbides present in the annealed state of 18/4/1 and 6/5/4/2 steels is taken into solution. If, after this first hardening operation, as well as after subsequent tempering treatments, the steel is re-hardened, the final austenitic grain size may be considerably larger than that obtained during the initial hardening, since the now more widely spaced carbide particles are less effective in obstructing grain growth. Once a "fish scale" is formed, only hot-working of the steel will eliminate it, but annealing, prior to re-hardening, at such a temperature that a sufficient number of carbides is precipitated from solid solution, would appear to prevent this phenomenon.

Full annealing is usually carried out if re-hardening is required, but sub-critical annealing at  $750^\circ\text{C}$ ., and above, for one hour, has been found by the author to prevent the development of this defect in re-hardened 18/4/1 and 6/5/4/2 steels. Fig. 29 shows a 6/5/4/2 steel with an intercept grain size of 3.5. A fracture of this steel, showing "fish-scale," is to be seen along with that of a sound one in Fig. 30. A well hardened 18/4/1 or 6/5/4/2 high speed steel is usually found to have an intercept grain of 13-16. The presence of large grains in a high speed steel tool results, as in all metals, in a reduction in toughness.

## TOOL PROCESSING DEFECTS

### Structurally Faulty Welds

Resistance flash-butt welding is usually used to join the high speed steel portion to the mild steel tool shank.

TABLE VI.—TEMPERATURES OF TRANSFORMATION OF 18/4/1 STEEL ON HARDENING.

Stage	Temperature ( $^\circ\text{C}$ .)	Stage	Temperature ( $^\circ\text{C}$ .)
$M_s$ Point	220	40% Martensite	145
10% Martensite	195	50% Martensite	120
20% Martensite	180	60% Martensite	95
30% Martensite	160	70% Martensite	55

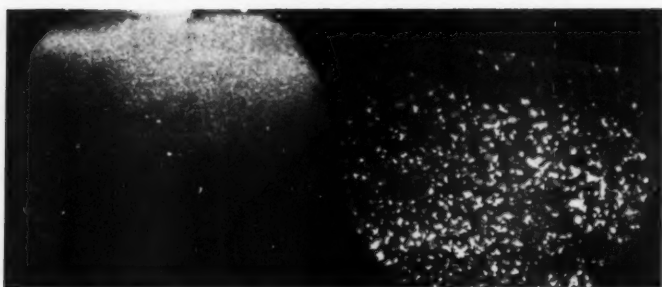


Fig. 30.—Fracture of a sound 6/5/4/2 steel and one showing a "fish-scale."

Unsuitable welding techniques may result in the production of the following defects:—

- The formation of a eutectic structure in the disturbed zone of the high speed steel portion. As already mentioned in the point dealing with insufficiently hot-worked steels, the presence of carbide segregation makes high speed steel very prone to this defect.
- The formation of areas of lower bainite at the junction of the high speed and shank steels after full annealing of the welded component.

Fig. 31 shows the structure of a sound weld; Fig. 32 the eutectic structure in the disturbed zone of the high speed steel portion; and Fig. 33 a faulty weld containing areas of lower bainite at the junction of the high speed and shank steels.

The influence of eutectic carbides in the structure of high speed steel has been sufficiently covered in other parts of this article, and requires no further explanation. The presence of bainite is detrimental only to the subsequent machining of the welded part. Full re-annealing, as for high speed steel, would reproduce the same structural condition. Therefore, tempering of the bainite only is necessary in order to soften the weld for ease of machining. Any temperature between 650° and 700° C. should produce a satisfactory hardness condition.



*Reduced 1/2 linear in reproduction.*

Location	Hardness	
	V.P.N.	R <sub>c</sub>
Disturbed zone	289	28
High speed steel	239	20

Fig. 31.—Sound weld in 18/4/1 steel, annealed. × 500

## Grinding Defects

Most tools are ground to final size or shape after full heat-treatment. The defects which may be produced in these operations are due either to the use of unsuitable grinding wheels or to a faulty technique in grinding the tools. The presence of areas of excessive carbide segregation and of untempered martensite makes the steel more prone to grinding hazards.

### Change in Structure and/or Hardness

This defect, commonly called "burning," leaves bluish discoloration on the surface of the tool. When the heat generated during grinding raises the temperature above the

tempering temperature, but not above the A<sub>1</sub> point, softening of the tool occurs. This can, in many cases, be determined by a hardness test. On microscopical examination the affected groundmass will etch darker than the remainder. (A groundmass that is softer due to a carbon gradient etches lighter).

When the heat generated during grinding raises the temperature above the A<sub>1</sub> point (about 820° C.—835° C. for both 18/4/1 and 6/5/4/2 steels), re-hardening of the steel takes place. Fig. 34 represents a section of a fully heat-treated tool which was re-hardened by the heat generated during grinding. The part etching white is



Location	Hardness	
	V.P.N.	R <sub>c</sub>
Disturbed zone	381	39
High speed steel	249	22

Fig. 32.—Faulty weld in 18/4/1 steel, annealed: eutectic structure present. × 500

a re-formed martensite-austenite; adjacent to it is a transition zone with a re-formed martensite-austenite in the grain boundaries; this is followed by the dark-etching over-tempered martensite blending into a normally tempered structure. The size of these zones is a function of the magnitude of heat generated and its depth of penetration.

The presence of re-formed martensite-austenite and of high stresses in a tool will most probably cause spalling or snipping of the affected part.

### Cracks and/or Stresses in the Tool

The presence of a crack and/or stresses can be attributed to a rapid and localised volume change of steel



due to heat produced by either excessive grinding or the use of improper grinding wheels. The danger to a tool which was highly stressed during grinding is that the addition of stresses produced by machining may exceed the rupture strength of the steel and result in the failure of the tool.

The presence of stresses in a ground tool can be revealed by hot etching the tool in a 50% aqueous solution of hydrochloric acid, at a temperature of 70° C., for 10-15 minutes. The presence of low stresses is indicated by the production of single grooves, as in Fig. 35, usually running transversely to the direction of grinding. The presence of high stresses is revealed by the production of a checker-work pattern of grooves, as indicated in Fig. 36. It should be pointed out that this test is a destructive one.



Location	Hardness	
	V.P.N.	R <sub>c</sub>
Bainite ... ..	476	47
High speed steel ... ..	246	21

Fig. 33.—Faulty weld in 18/4/1 steel, annealed: lower bainite present.  $\times 500$

Most toolmakers are aware of the grinding dangers arising from the use of unsuitable grinding wheels (usually too fine and hard), too high a rate of metal removal, or a faulty technique. When they become blunt, however, tools are re-ground by the user, and a further opportunity arises for the tool to be damaged to such an extent as to cause its failure.

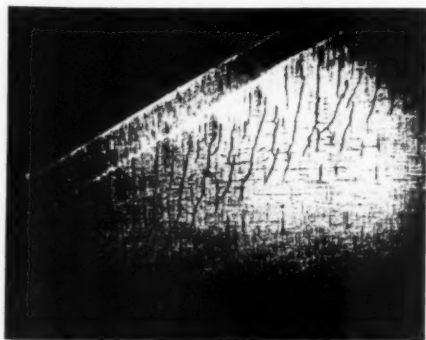
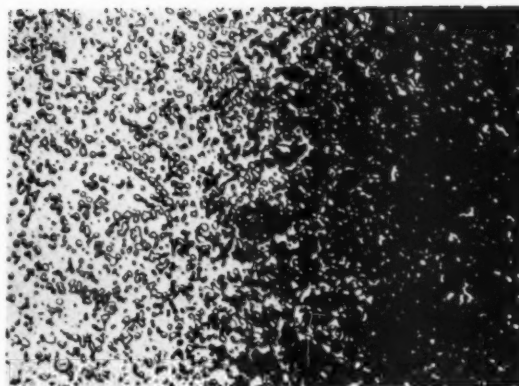


Fig. 35.—The presence of light grinding stresses in fully heat-treated 18/4/1 steel revealed by hot etching.  $\times 4$



Location	Hardness	
	V.P.N.	R <sub>c</sub>
Re-formed martensite-austenite ... ..	782	63
Transition zone ... ..	690	60
Over-tempered zone ... ..	762	62.6
Normal structure ... ..	894	67

Fig. 34.—Fully heat-treated 6/5/4/2 steel re-hardened by grinding.  $\times 400$

The author hopes that the foregoing description of some of the metallurgical defects in high speed steels may be helpful in drawing the attention of steelmakers, toolmakers and tool users (re-grinding) to those aspects of high speed steels over which they exercise control. If high speed steel tools are to play their full part in increasing productivity, they should all realise the problems involved and contribute their share to the making of sound tools and their correct use.

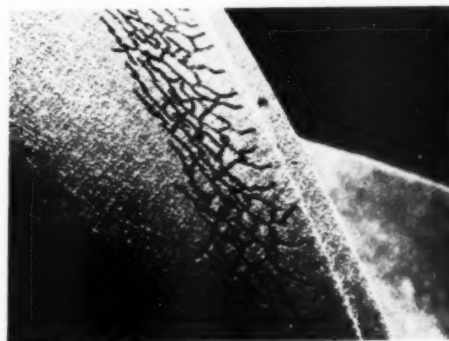


Fig. 36.—The presence of heavy grinding stresses in fully heat-treated 18/4/1 steel revealed by hot etching.  $\times 4$

#### Acknowledgments

The author wishes to thank the Board of Directors, The Sheffield Twist Drill and Steel Co., Ltd., Sheffield, for permission to publish this article\*. He is also indebted to Mr. Chas. Pillinger, B.Met., Research Department, The Sheffield Twist Drill and Steel Co., Ltd., for the preparation of the photographs and photomicrographs featured in it.

\* This article is to be reprinted, and copies will then be available on application to the Publicity Department, The Sheffield Twist Drill Co., Ltd., Sheffield.

## Translations Available

SOME of the translations announced in List 23 of the Co-operative Translation Service are listed below. Translations identified by a number may be obtained from the Service at The Iron and Steel Institute, 4, Grosvenor Gardens, London, S.W.1. Those identified by the letter BT followed by a number are made available by Mr. H. Bratcher, from whom they may be obtained at P.O. Box 157, Altadena, California, U.S.A.

- | No.      | Title   |
|----------|---|
| 589      | FACKERT: "Structure of Scale on Hot Rolled Strips and Sheets." <i>Stahl u. Eisen</i> , 1955, Dec. 15th, 1705-1710. (£3 10 0).   |
| 596      | SAILLARD: "Investigations of Reinforcing Steels with an Elastic Limit of 60 kg./mm. <sup>2</sup> Determination of a 'Tor-60' Steel." <i>Travaux</i> , 1954, Sept., 437-451. (£5 10 0).                              |
| 597      | RUHL: "American Tests on Brittle Fracture and the Resulting Conclusions on Testing of Brittle Fracture." <i>Arch. Eisenhüttenwesen</i> , 1954, Sept.-Oct., 421-433. (£10).  |
| 628      | TsNIITMASH (Central Scientific Research Institute of Technology and Engineering): "Testing and Properties of Heat-resisting Materials." Mashgiz, Moscow, 1957 (vol. 79 of series), 8vo. (£3).                       |
| 729      | BELOUS: "Welding of Gears under Protection of Carbon Dioxide." <i>Svarochnoye Proizvodstvo</i> , 1956, 20-22. (£1 15 0).  |
| 767      | MULLER and MARX: "Results of Testing the Operation of Blooming Mills. Part I—Methods used in Measuring the Characteristic Data in Rolling Blooms." <i>Stahl u. Eisen</i> , 1957, Oct. 31st, 1577-1582. (£3).        |
| 780      | NOVIKOV: "Effect of Surface Hardening by Heating with Mains Frequency Currents on the Properties of the Working Rolls for Cold Rolling." <i>Metallovedenie i Obrabotka Metallor</i> , 1956, June, 36-47. (£5 10 0). |
| 789      | CAI <i>et al.</i> : "The Training of Railway Personnel in Steelworks." International Transport Conference, Sept., 1957, London. (£7).   |
| 853      | KLARDING: "Selection of Tool Steels for Hot Working." <i>Metall</i> , 1958, Jan., 12-20. (£4 10 0).   |
| 857      | POPOV: "The Technological Requirements for Automation of Wire and Wire Products Production." <i>Stal</i> , 1957, Dec., 1128-1130. (£2).   |
| 882      | FERRO and MONTALENTI: "Variations in the Magnetic and Mechanical Properties of Iron Caused by Hydrogen Solution." <i>Il Nuovo Cimento</i> , 1957, Apr. 1st, 842-852. (£3).  |
| 889      | SEVERING: "Design and Operational Results of a Modern Continuous Train Rolling Medium Strip." <i>Stahl u. Eisen</i> , 1958, Feb. 20th, 205-214. (£6).   |
| 893      | KOHLER: "The Hydrocyclone as Part of the Water Circulation System in an Integrated Steelworks." (Abridged). <i>Stahl u. Eisen</i> , 1958, Feb. 20th, 235-239. (£2).   |
| 900      | KOCH <i>et al.</i> : "The Formation of a Cubic Nitride in Aluminium-containing Steels." <i>Arch. Eisenhüttenwesen</i> , 1956, Nov., 701-706. (£3 10 0).   |
| 907      | GUESSEIER and CASTRO: "Simple Machines for the High Temperature Testing of Steels and Alloys." <i>Rev. Met.</i> , 1957, (2), 101-106. (£3 15 0).  |
| 910      | NEFF: "A New Counter Goniometer for Determining the Texture of Sheet Materials." <i>Z. Metallkunde</i> , 1956, Sept., 646-649. (£2 5 0).  |
| BT 3854* | TOLSTOGUZOV: "Mechanical Nature of Temper Brittleness." <i>Metallovedenie i Obrabotka Metallor</i> , 1956 (8), 28-30. (£3.25).  |
| BT 4090  | KURCHATOV: "Ferrocake and Ore-coal Briquets." <i>Stal</i> , 1957 (2), 103-105. (\$4.80).  |
| BT 4094  | KRIVOSHEEV and LEV: "Non-metallic Inclusions in Magnesium-treated Iron." <i>Lit. Proizv.</i> , 1957 (11), 18-19. (\$4.80).  |

\* Mr. Bratcher will send this improved re-issue translation No. 3854 free of charge to all holders of the original version, upon request.

- BT 4115 PETROV: "Arc Welding with Various Shielding Gases." *Svarochnoye Proizv.*, 1957, Aug., 6-10. (\$5.80).
- BT 4131 MOROZOV *et al.*: "Taking Samples from Semi-finished Steel for Hydrogen Analysis." *Zavodsk. Lab.*, 1956 (7), 867-869. (\$2.30).
- BT 4139 EMINGER, KINSKY and KLETECKA: "Importance of Vacuum Casting of Steel to Industrial Practice." Part II. *Hutnické Listy*, 1957 (8), 755-768; also *Neue Hütte*, 1957 (10), 590-600. (\$11.00).
- BT 4149 PAISOV and So YUN HO: "Mechanical Properties of Some Ultra High Strength (Structural) Steels." *Metallovedenie i Obrabotka Metallor*, 1958, Feb. 2-6. (\$4.50).
- BT 4141 HOVGARD and JENSEN: "On the Oxygen Content of Wustite in Equilibrium with Various Gas Phases." *Jernkontorets Ann.*, 1956 (7), 467-492. (\$13.40).

## Welding Publications

TECHNICAL papers delivered by members of the staff of Quasi-Arc, Ltd., during recent months, are now available on application to the firm at Bilston, Staffs. They include "The Expanding Field of Automatic Arc Welding," "Welding Processes and their Applications," and "High Production with Automatic Arc Welding," by MR. J. A. LUCEY, Manager of the Company's Automatic Welding Development Department; "Welding Metallurgy and the Testing of Welds," by MR. P. F. WILKS, Metallurgical Services Manager; "Gas Shielded Continuous Electrodes," by DR. W. E. FREETH, Manager of Automatic Welding Processes, Materials Development Laboratory; "Selection and Use of Arc Welding Processes," by MR. E. FLINTHAM, Sales Manager; "Welding," by MR. G. C. POXON, Electrical Development Manager; "Fusarc/CO<sub>2</sub>," by MR. E. J. MITCHELL, Metallurgical Research Manager; "Recent Developments in Welding Processes for Ferritic Steels," by MR. P. L. J. LEDER, Director of Welding Research; and "Fusarc/CO<sub>2</sub>," jointly by MR. MITCHELL and MR. LEDER.

## Large Vacuum Arc Furnace

THE new consumable electrode vacuum arc furnace ordered by William Jessop & Sons, Ltd., from W. C. Heraeus, of Hanau, Western Germany, through their U.K. agents, Fleischmann (London), Ltd., will be the largest of its kind in Europe. It will make possible the production of ingots up to 24 in. in diameter and 3 tons in weight, and will be used for the manufacture of Vacumelt steels and Hylite titanium alloys.

Among the advanced design features of the new furnace are fully automatic control and special attention to safety devices. W. C. Heraeus claim to be the world's leading makers of vacuum arc furnaces, having completed some sixty plants, including ten for ingots over 1 ton. The latter include several large titanium arc furnaces (for ingots of 25 in. diameter) for the Metals Division of Imperial Chemical Industries, Ltd.

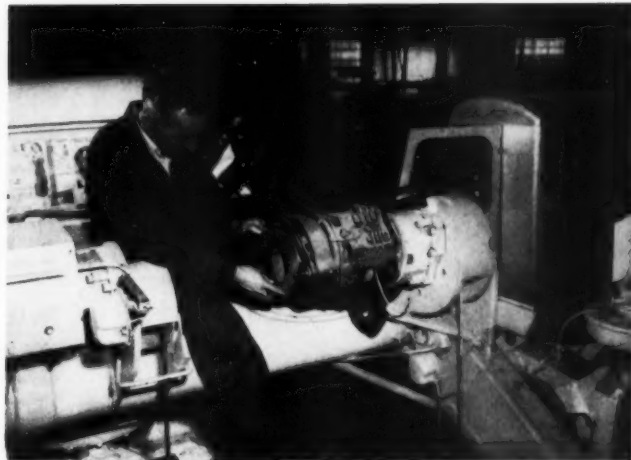
## Changes of Address

METROPOLITAN-VICKERS ELECTRICAL CO., LTD., announces that the postal address of the Company's Sheffield District Office is now 9, Market Place, Sheffield 1. The telephone numbers, Sheffield 23114/5/6/7 and 27848 remain unchanged.

THE Hull Branch Office of British Insulated Callender's Cables, Ltd., is now: 49, Mytongate, Hull (tel.: 16470 and 16367).

# Sintered Metal and Cerametallic Friction Materials

## New Ferodo Manufacturing Venture



Fitting a Ferodo metal brake disc to the hoist motor of a Letourneau Westinghouse D type Tournapull Scraper.

**A**N important step in the development in this country of sintered metal and cerametallic friction materials for the control and transmission of power in road and rail vehicles, excavators, cranes, earth-moving machinery, tractors, and agricultural machines, has been taken by Ferodo, Ltd. The company has entered the field of sintered metal production on an ambitious scale, providing sintered facings for new clutch and brake designs as well as a comprehensive range of replacement metallic facings. It has had the benefit in the design of production plant of the experience of the S. K. Wellman Company of America, who largely pioneered the application of sintered metals to the brake and clutch lining industry, and in collaboration with

whom Ferodo is already manufacturing these products on full-scale plant at its works at Chapel-en-le-Frith.

Until now conventional friction materials, based on asbestos, have fulfilled all the demands made upon them. Ferodo sintered metals will not replace asbestos-based products, but they will make possible the design of clutches capable of sustaining duties beyond the scope of conventional linings and facings. They will also provide a Ferodo quality for replacement linings and facings on heavy equipment, mainly of American design, which have standardised metallic facings for certain brake and clutch applications.

### Sintered Metal Linings

Sintered metal linings are produced by the compression and partial fusion of very fine particles, mainly of powdered metals. Their physical properties, derived from their constituent metals, give them, under certain conditions of high unit loading, longer life and more stable friction than asbestos-based materials. They are naturally more expensive than conventional materials, but their use is justified by their performance under conditions which are beyond the range of conventional materials, and where considerations of space make them essential.

The facings are flat discs or segments, generally built on to steel backing or core members, and may be very thin by traditional standards. The complete units may then be mounted by riveting; more frequently, the core member may be geared or splined to transmit torque. They are supplied for operation dry or in oil-immersed conditions, and give excellent service against normally accepted steel or alloy mating members, i.e. with a Brinell hardness number of 160 or more in dry applications; a lower Brinell number is acceptable for oil-immersed conditions. Cast steel is unsuitable for use as a mating member, since it is liable to be scored by whatever friction material is used.

Since dies and tools are an indispensable part of the manufacturing process, the maintenance of an economical price level is dependent on quantity production when special sizes are required. Furthermore, supple-



Removing electric bell furnace, after sintering, to reveal the container.



Hydraulic press for compacting metal powders.

mentary features like spline hardening, grooving and slotting increase the cost of the part.

#### Advantages of Sintered Metal Friction Materials

Because sintered metals absorb energy and conduct heat faster than most organic or mineral friction materials, they can be used under conditions which would lead to excessive temperatures for asbestos-based materials. As energy in the form of heat can be dissipated through the friction surface and the mating member, both surfaces run cooler and, in consequence, the life is increased. Additionally, less distortion and heat checking of the opposing member occur.

Although sintered metals possess a lower coefficient of friction than conventional asbestos-based facings, that coefficient is maintained through a far wider range of temperature and pressure variations, a characteristic which gives smooth engagement and is particularly useful in protective and torque-limiting clutches.

The metallic matrix is not affected appreciably by heat, cold or dampness, and quickly recovers from contamination by oil or solvents. On a dry clutch, the clutch action itself clears away foreign substances or fluids and, in doing so, restores the facing's coefficient of friction. Its structure being unaffected by oil, sintered metal is ideal for oil-immersed clutches, although naturally with a lower coefficient of friction than when operating dry.

Sintered metal friction materials can withstand higher normal pressures than asbestos-based materials without performance being affected. This property, together with the higher energy dissipation rates which can be catered for, makes possible the design of smaller, lighter, and more compact clutches for high energy absorption applications.

Ferodo sintered metal for dry applications is supplied with a special surface finish to ensure swift and smooth bedding-in of the surface. This is not necessary for grooved facings operating in oil, which are prepared with a normal machined finish.

#### Applications

In heavy-duty clutches and brakes, sintered facings give consistent operation under arduous conditions. These applications include the steering clutches of crawler tractors, master clutches of all types of tractors, clutches for road rollers, steering clutches for track-laying fighting vehicles (tanks, etc.) and for a multitude of other clutches and brakes in all types of earth-moving equipment.

Sintered facings are also useful in other clutches where consistent engagement characteristics are required. These include the multi-plate oil-immersed clutches employed in automatic gear boxes for all types of road and rail vehicles, and also the clutches which lock up the torque converters used in rail-car propulsion. Torque-limiting clutches and tensioning devices also fall into this category, as do the host of small instrument clutches where smooth take-up or break-away is essential.

In most designs of electro-magnetic clutch and brake the air gap of the magnet is changed as the friction surface wears. Even the smallest change in the gap affects the clamping force considerably, and the wear of the friction facings must therefore be kept to an absolute minimum if excessively frequent adjustment is to be avoided. Sintered metal facings, which can be prepared with only a very thin layer of very wear-resistant friction material, enable the full use to be made of the available friction material whilst giving extremely good life between adjustments.

In compact clutches, where small size and weight is important, the ability of sintered metal to work at high pressures and energy ratings enables very appreciable reductions to be made to the size and weight of the clutch unit at the design stage. This is of particular importance for the many aircraft clutch applications, e.g. actuators, and has also an obvious advantage in such cases as racing-car clutches, where weight is at a premium.



Trimming a set of sintered discs on a vertical boring machine.



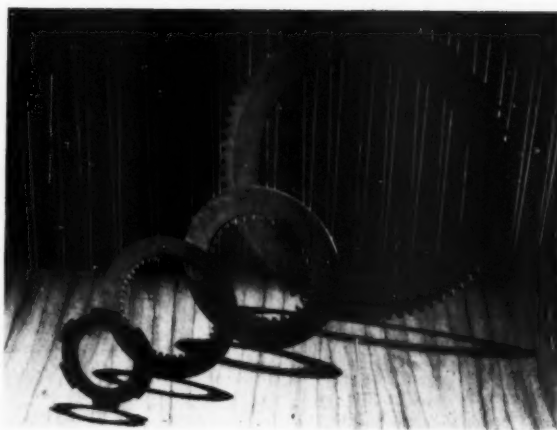


Left:

Ferodo sintered metal segmental facings formed on individual steel backing segments.

Right:

One iron-based and three bronze-based Ferodo sintered metal gearcut facing discs.



### Types of Product

The basic processes involved in manufacture are as follows. The dry metal powders are accurately mixed and blended. They are then cold compacted at high pressures. The compacts are next assembled on their backings or cores which have already been prepared so as to assist the formation of a bond between plate and facing. The assembly, of compact and backing plate, is then sintered in a reducing atmosphere at temperatures up to 1,000° C. After sintering, the assemblies are finished by grinding, edge trimming, drilling, branding and other necessary finishing operations. They are also finally inspected for dimensional accuracy before despatch. Brief particulars of the various grades are given below and their physical properties in Table I.

#### Sintered Metal Linings

Ferodo SM1 is a general-purpose bronze-based sintered material for dry and oil applications where a reasonably high coefficient of friction is required and energy conditions are not unduly severe. Typical

applications include master clutches, transmission clutches, steering clutches and various accessory clutches in earth-moving, ordnance and industrial applications.

Ferodo SM2 is a bronze-based sintered material which has been developed for oil-immersed applications requiring smooth, gradual engagement; for example, automotive automatic transmissions.

Ferodo SM3 is a bronze-based sintered material which is especially suited to dry heavy-duty applications such as master or engine clutches on trucks and earth-moving equipment, and on tractor steering and power control unit brakes. It contains several dry lubricants giving it excellent heat-resistant and anti-seizing properties.

Ferodo SM4 is an iron-based sintered powder material with excellent heat-resisting qualities. It is used as a lining to protect costly parts, such as flywheels and pressure plates from heat damage and wear. Ferodo SM3 may be used to work against an SM4 mating surface. The friction values remain much the same as when SM3 is working against alloy cast-iron, but the combination offers some advantage in wear resistance under particularly heavy duty conditions.

Ferodo SM5 is a bronze-based material designed for applications involving long slip periods. It provides for applications in seals, lubricated bearings and tension control clutches where consistency of friction level and low wear rate are the main requirements. It contains a relatively high percentage of lead, which limits its operating temperature to about 500° F. (260° C.).

Ferodo SM6 is again a bronze-based material intended for operation in oil. Its relatively high friction coefficient and flat torque curve make it suitable for applications where smooth engagement must be coupled with a relatively high capacity.

#### Backing Plates

Ferodo, Ltd., can supply sintered metal facings complete with cores or backing members, or they can sinter the facings on to parts supplied by the customer. Cores or backing members can be produced from any steel which can be copper-plated. For some duties the use of a fairly high carbon type of spring steel is advantageous, especially where the core member is splined or gearcut to transmit the torque. The process used in applying Ferodo sintered metal to a core fully anneals

TABLE I.—PHYSICAL PROPERTIES OF SINTERED METAL LININGS.

Ferodo Designation	SM1	SM2	SM3	SM4	SM5	SM6
Friction Value for Design Purposes						
(dry) . . . . .	0.24	—	0.26	—	0.23	—
(oil) . . . . .	0.05	0.04	—	—	—	0.07
Static Friction Value						
(dry) . . . . .	0.35	—	0.34	—	0.26	—
(oil) . . . . .	0.38	—	0.26	—	0.28	—
	0.10	0.12	—	—	—	0.10
	0.12	0.14	—	—	—	0.12
Dynamic Friction Value						
(dry) . . . . .	0.29	—	0.30	—	0.24	—
(oil) . . . . .	0.32	—	0.33	—	0.21	—
	0.06	0.05	—	—	—	0.09
	0.08	0.07	—	—	—	0.09
Ultimate Tensile Strength						
(lb./sq. in.) . . . .	6,500	10,200	6,500	12,500	7,500	6,500
(kg./sq. cm.) . . . .	470	720	460	880	530	460
Ultimate Shear Strength						
(lb./sq. in.) . . . .	8,500	11,400	9,300	13,400	10,400	9,000
(kg./sq. cm.) . . . .	600	800	650	940	730	630
Cross Breaking Strength						
(lb./sq. in.) . . . .	17,500	21,000	19,100	16,300	18,200	18,500
(kg./sq. cm.) . . . .	1,230	1,480	1,340	1,150	1,280	1,300
Density						
(lb./cu. in.) . . . .	0.216	0.234	0.216	0.202	0.227	0.214
(g./c.c.) . . . . .	6.0	6.5	6.0	5.6	6.3	5.9

the steel, and spline strength should therefore be calculated on the basis of the steel fully annealed.

Standard cores or backing members are made from :—

Backing plates or plain core plates.

Core plates gear cut.

Mild steel (En 2).  
En 6 (0.3-0.4% C), i.e.  
equivalent to SAE1035  
En 42.

Special gear-cut plates of automatic transmission type.

Special applications.

En 42.  
En 43F.

#### *Cermetallic Friction Materials*

These are broadly similar to the sintered metal

products already described, except that they contain a proportion of ceramic powder which increases their heat and wear resistance, and raises their friction level. These advantages are to some extent offset by a tendency to abrasiveness and by the higher cost resulting from manipulating difficulties inherent in the material. The latter consideration makes it necessary to form the cermetallic friction material as a circular pad or button in a steel cup. A number of such buttons can then be riveted round the supporting member. The principal applications for cermetallic materials are the clutches of earth-moving machinery, agricultural machinery and disc brake pads for aircraft.

## Germanium Resistance Thermometer

A GERMANIUM resistance thermometer having high sensitivity and exceptional stability in the temperature range near absolute zero has been developed by J. E. Kunzler, T. H. Gaballe and G. W. Hull of Bell Telephone Laboratories. Once calibrated, this thermometer is reproducible to better than a few ten thousandths of a degree at the boiling point of helium (4.2° K.), even after repeated cycling from room temperature. Such characteristics indicate that this thermometer might be useful for the accurate measurement of temperatures in outer space, when mounted in a suitable space vehicle.

Continued emphasis on low-temperature research has highlighted the need for a thermometer which would indicate low temperatures accurately and reliably, and would not need continued recalibration. Such a device would be of great help in low-temperature calorimetric work. The germanium resistance thermometer meets these specifications.

The heart of this thermometer is a very small "bridge" cut from a single crystal of arsenic-doped germanium. Actual size of this bridge is about  $0.025 \times 0.020 \times 0.210$  in. Current and potential leads are attached to the bridge, and it is supported in a strain-free manner in a platinum-glass enclosure containing a small amount of helium gas to aid in thermal conduction. The resistance is determined by measuring the potential drop when a

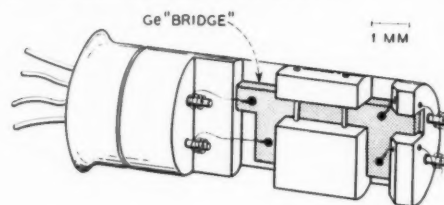


Diagram showing internal construction of the germanium resistance thermometer

small (approximately 10  $\mu$ A.) known current is passed through the bridge.

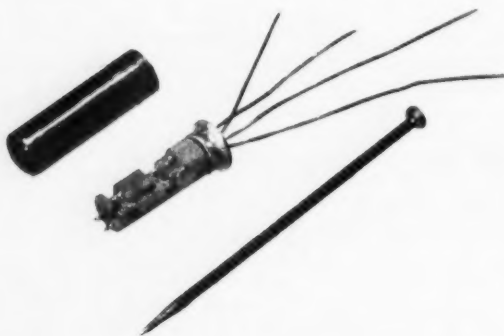
Germanium can be doped with arsenic to produce a high and fairly constant temperature coefficient of resistance at temperatures near the boiling point of helium. For example, a typical thermometer made at Bell Laboratories had a resistance of about 1 ohm at room temperature, 14 ohms at 10° K. and 216 ohms at 2° K. Both the temperature coefficient and the actual resistance vary widely with minute changes in the amount of doping, making it possible to fabricate a thermometer having any of a wide range of characteristics. Such a thermometer will retain its calibration despite repeated cycling from 300° K. to 1° K.

To avoid excessive heating when measurements are being made, the resistance of the thermometer should be kept as large as possible. However, for simplicity in measurements, a low resistance is desirable. For a specific application, a compromise can be reached by controlling the doping of the germanium crystal.

These resistance thermometers are not available from Bell Telephone Laboratories, but a number of them are being turned over to the Calorimetry Conference for testing. If this Conference finds that they have wide usefulness, efforts will be made to interest a qualified manufacturer in making them commercially available.

### Medal Award

THE West of Scotland Iron and Steel Institute has awarded the Riley Medal for the undernoted paper: "Development of a Manganese-Chromium-Molybdenum-Vanadium High-Tensile Weldable Steel for Pressure Vessels," by W. Barr and I. M. Mackenzie, which was presented during session 1956-57.



The germanium resistance thermometer photographed alongside a pin.

# Fabrication of an All-Welded Gas Main

**A**N all-welded gas main which has a length of approximately 10,000 ft. has been fabricated by the Tees Side Bridge and Engineering Works, Ltd., with the aid of welding equipment supplied by Quasi-Arc, Ltd. The main is being used to carry blast furnace gas from the Cleveland works of Dorman Long (Steel), Ltd., to the company's steel plant at Lackenby, where it supplies reheating furnaces, soaking pits and other plant. It originates in a 9 ft. diameter header pipe, and the distribution pipes at Lackenby are in diameters of 4 ft., 3 ft. 6 in., and 3 ft. The major portion of the main has a diameter of 5 ft. 6 in. Expansion joints are incorporated in the construction at intervals of 300 ft., and manholes were provided to facilitate internal site welding and inspection.

Pipe sections were pre-fabricated in lengths varying between 30 and 40 ft. The major portion of the main was fabricated in 33 ft. sections, each composed of four 8 ft. 3 in. strakes of  $\frac{3}{8}$  in. wall thickness, one plate to the round, and these, when welded together, formed a pipe section weighing about four tons. This was then transported to the site for erection and welding in position. Plate preparation took the form of machining to template with squared edges for shop welding and bevelled edges where site joints occurred. The plates were rolled into shape after the edges had been pre-set in a hydraulic press. For the straight sections of the 5 ft. 6 in. main, four of the cylinders thus formed were assembled and tack-welded together, with no gap at the joints, to form a 33 ft. section. Each section was then mounted on a roller bed ready for welding with a combination of the Fusarc and Twinarc processes.

The internal sealing runs were applied manually by the Twinarc process, using 6 s.w.g. Twinarc R twinned electrodes at 190 amp. per electrode. The process was chosen for this application in view of the fact that it increases deposition rate and enables welders to match the production of the Fusarc equipment more economically. The Fusarc head was mounted on an elevating arm attached to a column. These were in turn mounted on a trolley which could travel along a 4 ft. 8  $\frac{1}{2}$  in. gauge track at welding speeds infinitely variable between 5 and 60 in./min. The rotating equipment turned the work pieces at similar speeds. Both longitudinal and circumferential welds were completed in one pass at 20 in./min.

Two sets of roller beds were positioned alongside the track, which was of sufficient length to enable the welding equipment to traverse along both roller beds. Thus, while one pipe section was being externally welded, another was being internally sealed. On completion of both these operations, the welding machine traversed to the other roller bed and performed external welds on the second section. A very high duty cycle was obtained, and this ensured that the automatic installation was used with maximum economy.

Pipe bends and branch sections were also welded in the shop. Welding was carried out manually using 10 s.w.g. and 8 s.w.g. Quasi-Arc Vortic electrodes. The plate preparation for these welds was the same as that used for the site welds—vee-edge with a 60° included angle,  $\frac{1}{8}$  in. root face and  $\frac{1}{16}$  in. root gap. Only the root pass was deposited with 10 s.w.g. electrodes, all filling passes and the inside sealing run being made with 8 s.w.g.



General view of the welded gas main.

Welding together the sections on site was also carried out with Vortic electrodes, using the same preparation. In some parts of the Cleveland Works, where the main passes over working areas at high level, it was considered desirable to minimise *in situ* welding. Two or three sections were therefore welded together on the ground and the resulting section was lifted into position by mobile cranes. By adaption of the erection technique to meet the prevailing conditions throughout the length of the main, work was able to proceed smoothly.

## Turbine Gear Machinery Orders

OVER the past ten years, the David Brown Machine Tool Division of Sherborne Street, Manchester, has made and supplied more large turbine gear-cutting machines than any other manufacturer in the world. Despite fierce competition from the U.S.A., Germany and other manufacturers in Britain, orders for 50 machines, together weighing 3,000 tons and worth over £3 million, have been received from customers in this country, Japan, Australia, America, France, Italy, Denmark, Germany, and Switzerland. An order for the fifty-first has just been placed by a Swedish electrical engineering concern.

The machines concerned, the largest in the David Brown range, weigh between 20 and 120 tons each, and are capable of cutting turbine gears from 10 in. to 216 in. diameter. The specification of accuracy against which they are supplied is in many respects a considerable improvement over the recognised British Standard.

## New Film for Steel Industry

A FILM about the steel industry in Britain today is to be made for the British Iron and Steel Federation. It will be an entertaining technicolour miniature film running about 30 minutes, and the most comprehensive undertaken by the industry in the past ten years. Professional actors will portray economic life and the opportunities in the industry. This type of miniature film is a new technique in documentary film making created by Martin Films who are making the film. Camera crews will visit steel centres in Wales, North-East England and Scotland. The film should be completed in the autumn.



General view of one of the eleven bays in the press shop.

**W**HEN two new plating plants with a total length of 480 ft. went into operation at the Luton factory last month, Vauxhall Motors' programme for doubling its production capacity was completed. The Luton developments have accounted for the major part of the £36 million spent by the company since 1954 on plant expansion and modernisation. Formerly the Luton plant produced both cars and commercial vehicles, and the small factory at Dunstable was used only for the manufacture of a limited number of non-current components. To permit a greatly increased scale of passenger car production at Luton, it was necessary to remove truck manufacturing operations to a new location. The decision was taken to enlarge the Dunstable plant to house all Bedford truck manufacturing and assembly activities except the production of steel cabs, which would continue at Luton.

The new passenger-car building at Luton is 1,450 ft. long  $\times$  900 ft. wide, and nearly half of it is of two storeys: there is also a basement of 150,000 sq. ft. and a pent-house of 83,000 sq. ft. It houses press shop, body building, paint and trim shops, and final assembly operations. Finished mechanical components are fed into it by conveyor from other buildings, which now contain several hundreds of the most up-to-date machine tools in the motor industry. The expansion and re-equipment at Luton involved the re-location of 3,000 existing machines and the installation of more than 2,000 new ones, costing £16 million.

#### The Press Shop

The press shop is probably the most spectacular part of the new car production building. Together with the steel stores it forms the foot of the letter L, which is the plan shape of the new building. This rectangular area is 882 ft. long by 400 ft. wide. The 100 ft. wide steel stores area runs along the full length of the foot, and is separated from the press shop by a wide gangway. It is unobstructed by steel girder support and the roof is of the cantilever type, curved, with the highest point 56 ft. above the floor level. Two crane runways 30 ft. above ground level, 100 ft. apart, permit the three 25-ton cranes to run the full length of the stores. Four entrances give

access for heavy road vehicles directly into the building: the entrances are tunnel-like structures with inner and outer doors, operated by photoelectric equipment so that only one door is open at a time, thus eliminating heat loss, or draughts.

The press shop consists of eleven bays, one of which is reserved for future development. Beneath nine of the bays there is a continuous basement in which are located nine conveyors for taking away the off-cuts of sheet steel to be baled by the baling plant. Steel girder networks support the under-drive presses mounted over the



One of the three transfer presses, each having nine stations, used for the production of many different pressed steel components at the rate of 900 per hour.

## Modern Press Shop at Luton

### Important Part of Vauxhall's Expansion Programme





Blanking sheet metal patterns from coiled steel strip. The machine is completely automatic in operation: it feeds itself.



One of the nine conveyors in the press shop basement which take off-cuts to the baler.

basement. Nine of the eleven bays are served by cranes (seven of 30-ton and two of 50-ton capacity), and a service gallery walk-way is built into the steel structure of the building at crane runway level. Natural daylight is admitted by the roof glass (87,714 sq. ft.), which represents 35% of the floor area, and artificial lighting is provided by a fluorescent tube installation.

There are twenty-six lines of presses, comprising 222 machines in all, three large multi-spot welding machines and four small ones. Of the presses, 118 are of the under-drive type, and the remainder conventional top-drive machines. They range in capacity up to 1,500 tons, and the heaviest weigh approximately 200 tons. Only three of the 222 are foreign built, and these are all nine-station transfer presses. A section of one of the bays is set aside for die maintenance operations, a Bliss bedding and spotting press, and three-lines of miscellaneous machine tools (twenty-five machines in all) being used for die repair and rebuild purposes. Other equipment in the shop and stores area includes four sets of Bronx rolls, six guillotines, two McKay coil feed blanking systems, nine blanking presses, two inspection department cribs and checking fixture storage areas, the baling plant, a spray sound-deadener plant, machine and electrical maintenance areas, and administrative offices.

The entire interior of the shop is painted in bright colours, in contemporary style. Royal blue, lime yellow, scarlet, white, cream, sea green and lemon are used on walls, girderwork, piping, etc., and the machines are all painted in battleship grey.

#### Press Feeding Systems

All but two of the presses are new installations. Many of them incorporate features of design which permit the use of loading and ejecting devices and other labour and time saving mechanisms, complete with built-in controls. All heavy and medium machines are equipped with developments of the well known "iron hand" device for unloading, and lines of machines are connected with portable band conveyors.

Many new loading devices are in use: these are mainly of the compressed air and piston type, synchronised with

the stroke of the press and operated by remote control. Some of the unloading devices are used in conjunction with turn-over mechanisms. Shuttle-loaders are also used in connection with multi-spot welding machines and double-acting presses which are to be found in Bay 1, which is set aside for the production of door assemblies (eight types) and luggage boot lid assemblies (two types).

The most technically advanced machines are the three Schuler transfer presses, which are used for the production of small components, such as fan pulleys, generator pulleys, and some deep drawn pressings. These machines are coil-fed and can produce at a rate of 900 components per hour. The die set-ups for fan and generator pulley manufacture are particularly interesting, as they include rubber dies for the expanding operation from which, subsequently, the V-belt grooves are formed. These grooves are held to 0.010 in. on true run-out.

Sheet metal in the form of coils up to 6 ft. wide can be blanked directly on this equipment, which employs a cone type carrier, a set of McKay rolls, a deep pit (20 ft.) for taking up slack, a timer roll, and a single acting clearing, blanking and shearing press. All these machines are linked under automatic control. Automatic stacking of blanks is installed for some of the operations.

#### Scrap Baling System

In the basement beneath the press shop, serving groups of lines of heavy presses, runs a network of eight apron-slat conveyors. Off-cuts are delivered by chutes on to the subsidiary conveyors which, in turn, deliver them to a main conveyor. This delivers on to a short run conveyor which leads into the baler. The conveyors are controlled by the baling machine operator, and a warning system, broadcast throughout the basement, indicates when conveyors are to be started up. The baling mach-

ine operator can also broadcast instructions over this loud-speaker system.

Bales weigh approximately 4-5 cwt., and are compressed to a standard width, though length and height can vary. This arrangement allows the bales to be conveyed by mechanical means without causing jamming in conveyors. They are delivered through a tunnel by means of a 126 ft. long conveyor of the pusher bar and twin-chain type, to the loading dock (a covered building separate from the main block) outside. An electromagnetic hoist lifts the bales on to waiting vehicles.

#### Conveyors and Stores

Three overhead monorail conveyors are installed to deal with the movement of door and luggage boot lid panels. One carries outer panels from the presses to the spray sound-deadener plant and back to the welding machines. The second circulates from the presses to the welding machines and back. The third conveyor carries welded assemblies from the press shop to the neighbour-

ing body-building shop. En route, it descends into a storage basement which has a floor area of 30,000 sq. ft.

Logically, the panel stores could be considered to be part of the press shop. This area covers 106,036 sq.-ft., and is divided into three sections: large panel storage; small component stores; and export pressings collection and collation area. The large panel storage area accommodates such items as roof panels, wings, bonnets and floor panels. These large items are packed into special pallets, designed for each panel, which are stackable to make full use of space. Smaller components are packed into stackable stillages. The export pick-up and collection area is partly loading dock and partly stores. Boxes, specially designed to accommodate panels, sheet metal components and sheet metal assemblies, respectively, are transported from the export boxing department to this area for loading. Tractor and trailer trucks take them back to the export despatch department, for checking and proofing. They are then sent to the docks for shipment to the overseas assembly plants.

## Hydraulic Rams in Corrosive Atmosphere

**A**FTER lengthy exposure to a highly corrosive, salt-laden atmosphere, the Fescolised rams used in special hydraulically-operated gangways at Southampton Docks have been inspected and found to be in almost perfect condition. The covered, telescopic gangways, which are used in embark and disembark passengers on the *Queen Elizabeth* and *Queen Mary*, lead into turrets mounted on rails so that they can be moved along the dockside and aligned in the correct position. The length of the gangway can be varied by telescoping one section into the other.

Each of the six gangways is fitted with two luffing and two slewing cylinders of the double-ended type, with piston rings fitted to the ram head. After the gangways were installed in 1949, it was found that the exposed surfaces of the steel rams were becoming heavily pitted by the corrosive action of sea spray, and the British Transport Commission specified that they should be sent to Fescol, Ltd., to be built-up by nickel deposition and given a surface finish of chromium.

To prevent all the gangways being taken out of service at one time, the 26 rams, which included two spares, were treated in batches over the period 1953-56. The

Fescolised rams were returned direct to T. H. & J. Daniels, Ltd.,—suppliers of the original hydraulic equipment—who then rebuilt the relevant cylinders and honed the bores. The work was carried out under the supervision of Mr. J. H. Jellett, O.B.E., Docks Engineer, British Transport Commission. Since being re-installed the rams have shown no trace of wear or corrosion, although some of them have been in use for nearly five years.

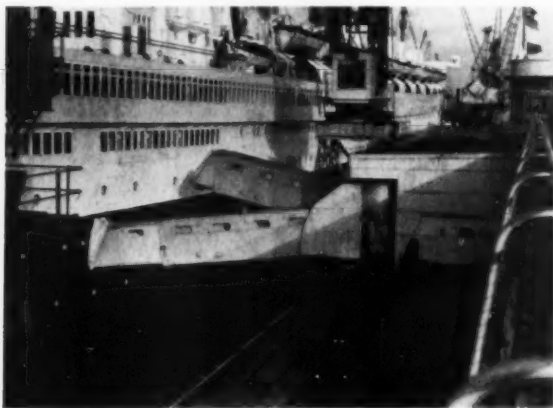
This treatment has since become almost standard practice with rams in docks and shipbuilding yards, where hydraulic presses are generally water-operated and are invariably exposed to salt atmosphere.

#### Automatic Polishing Machines

ELECTRO-CHEMICAL ENGINEERING CO., LTD., Woking, have been appointed exclusive sales representatives in Great Britain for all the products of Acme Manufacturing Company, Detroit. Acme have recently started to manufacture automatic and semi-automatic polishing machines in a new factory at Neu-Isenburg, near Frankfurt-am-Main, which was built for the purpose of supplying equipment to the European and non-dollar markets. Electro-Chemical Engineering are in a position to deal with enquiries and to import and install the machines: they will also carry stocks of essential spares.

#### Central Buying Department

NORTHERN ALUMINIUM CO., LTD., announce that a Central Buying Department, located at the Company's Head Office in London, has been established to co-ordinate purchasing policies within the Company and to negotiate for major items of equipment and bulk supplies of material. MR. D. A. CORBETT-THOMPSON, formerly Export Sales Manager, has been appointed Chief Purchasing Officer. The Buying Departments of the Company's three Works at Banbury, Birmingham and Rogerstone, Mon., will continue to function.



# NEWS AND ANNOUNCEMENTS

## Awards of Medals and Prizes

THE Council of The Iron and Steel Institute has announced the following awards for 1958:—

*Bessemer Gold Medal for 1958:* MR. W. F. CARTWRIGHT (Steel Company of Wales, Ltd.).

*Sir Robert Hadfield Medal for 1958:* MR. W. C. F. HESSENBERG (British Iron and Steel Research Association).

*Ablett Prizes for 1957:* £50 each to MR. C. E. H. MORRIS and MR. R. N. DALE (Steel Company of Wales, Ltd.), for their paper "Planning the Conversion of a High-lift Slabbing Mill to a Universal Mill." (*Journal*, April, 1957).

The two medals will be presented at the Annual General Meeting of the Institute, which is being held at 4, Grosvenor Gardens, London, S.W.1, at 2.45 p.m., on Wednesday, May 7th. The Ablett prizes are to be presented at a meeting of the Institute's Iron and Steel Engineers Group in the near future.

## Chemical and Petroleum Engineering Exhibition

BRITAIN'S first Chemical and Petroleum Engineering Exhibition, sponsored by the British Chemical Plant Manufacturers' Association and the Council of British Manufacturers of Petroleum Equipment, is being held at Olympia from June 18th-28th, 1958. No fewer than 250 exhibitor manufacturers have booked stands, and their exhibits already amount to 125,000 sq. ft.—occupying the whole of Olympia's two largest halls and galleries.

During the Exhibition The Institution of Chemical Engineers, in conjunction with The Institute of Petroleum, will stage a symposium on "The Organisation of Chemical Engineering Projects," and papers will be presented at four sessions spread over three days. This symposium will also form part of the 1958 programme of the European Federation of Chemical Engineering.

## Institute of Mining and Metallurgy Annual General Meeting

THE Annual General Meeting of the Institution of Mining and Metallurgy will be held on Thursday, May 15th, 1958, in the rooms of the Geological Society of London, Burlington House, Piccadilly, W.1. Visitors will be welcome at the open session at 5.15 p.m., when, following the Presentation of Awards, Mr. J. B. DENNISON will be inducted as President and will deliver his Presidential Address on "Productivity."

## Pressure Welding Conference

ORGANISED by the Department of Industrial Metallurgy, a Conference on "The Pressure Welding of Metals" will be held at Birmingham University on Thursday, 19th June, 1958. Professor E. C. Rollason will open the proceedings with an introductory survey and will be followed by Mr. J. A. Donelan, Research Laboratory, General Electric Co., Ltd., who will deal with "Industrial Practice in Cold Pressure Welding" and Mr. L. R.

Vaidyanath, Mr. M. G. Nicholas and Mr. D. R. Milner, Department of Industrial Metallurgy, whose subject will be "Pressure Welding by Rolling." In the afternoon, Dr. E. Holmes, Department of Metallurgy, Nottingham University, will speak on "Pressure Welding by Relative Movement between Surfaces," and the Conference will conclude with a general discussion.

An enrolment fee of 15s. will be charged, which will include the cost of lunch and light refreshments. The last day for receipt of applications for enrolment will be Thursday, 12th June: they should be addressed to the Secretary, Department of Industrial Metallurgy, University of Birmingham, Edgbaston, Birmingham, 15, and marked "Pressure Welding Conference."

## Magnesium in Aircraft

At a symposium jointly sponsored by the Magnesium Association and the Society of Aircraft Materials and Process Engineers, to be held on June 4th and 5th in Los Angeles, there will be a full discussion of existing and future potential uses of magnesium, particularly with respect to the part which the metal and the industry will be expected to play in the jet aircraft and missiles age. The first day's papers will be confined to technology and process control, with the two sessions of the second day devoted to papers prepared by workers in the aircraft field who are responsible for the incorporation of magnesium in aircraft and missiles.

Mr. P. A. Fisher, Deputy Chief Metallurgist of Magnesium Elektron, Ltd., is to present a paper on "Magnesium-Zirconium Alloys for Aircraft Structural Purposes," and, if time permits, a second paper on "Corrosion Protection Measures."

## M.I.T. Summer Schools

BECAUSE of the growing importance of light metal castings in American industry, the Massachusetts Institute of Technology is offering a special summer programme in "The Casting of Light Metals" during the 1958 summer session, from Tuesday, June 17th to Saturday, June 21st. A further special summer programme arranged for this year has the title "Metallurgical Applications of X-Ray Diffraction" and will be of two weeks' duration, from Monday, August 18th to Friday, August 29th.

## High Pressure Process Division

WOODALL-DUCKHAM CONSTRUCTION CO., LTD., announces that to meet the changing needs of the gas, oil and chemical industries, a High Pressure Processes Division has been established with Mr. H. S. CHEETHAM as Director-in-Charge. The new Division will concentrate upon the provision of complete plants for the production of gases suitable for town supply and chemical synthesis, etc., using modern high pressure techniques.

## Translation of Russian Journals

THE exclusive world-wide right to translate and publish complete English language editions of twenty Soviet scientific and technical journals has been granted to Consultants Bureau, Inc., under the terms of an agree-



ment reached between Mezhdunarodnaya Kniga, Soviet publications export agency, and the New York publishing firm. Journals covered by the agreement include publications in physics, chemistry, electronics, metallurgy, biology and medicine. Copies of photographs appearing in the journals are to be provided, so that the quality of reproduction will be satisfactory. All translations are to be so scheduled that by the end of 1958 none of the translated editions will be more than six months behind the publication of the original Russian journals.

Consultants Bureau, Inc., is also issuing a monthly guide to current Soviet research, entitled "Express Contents of Soviet Journals," which will make it possible for Western researchers to know the contents of Soviet periodicals published as recently as two months previously, and from two to six months before the complete translations are published. Further particulars can be obtained from Consultants Bureau Inc., 227, West 17th Street, New York 11, N.Y.

### Metallography Course

A SPECIALIST lecture course on "Modern Metallographic Techniques" will be held at the County Technical College, Wednesbury, on successive Wednesday evenings at 7 p.m., commencing June 4th, 1958. The programme is as follows:—

- "Developments in Optical and Electron Microscopy," by Dr. D. McLEAN (National Physical Laboratory).
- "Specimen Preparation," by Mr. J. A. ROBERTS (County Technical College, Wednesbury).
- "Hot Stage Microscopy," by Dr. M. J. OLNEY (Battersea College of Technology).
- "Micro-hardness Testing," by Dr. A. P. Miodownik (Battersea College of Technology).
- "Micro-radiography and Auto-radiography," by Mr. R. S. SHARPE (Bristol Aeroplane Co., Ltd.).
- "Colour Photomicrography," by Dr. G. PARKER (I.C.I. Research Laboratories).

The course fee is three guineas, and further particulars and a form of application can be obtained from the Registrar, County Technical College, Wednesbury, Staffs.

### Valve Manufacturing Project

OIL pipeline valves of a size and type previously manufactured only in the U.S.A. are currently being made by the David Brown Foundries Division, Penistone, to the order of the W.K.M. Valve Co. (Britain). Ltd. The valves are intended for use by the Shell Petroleum Company in Venezuela.

Although the Penistone company has had many years' experience in the production of steel castings for oilfield and refinery use, the manufacture of complete valves is an important new venture which has particular significance from the dollar-earning and dollar-saving point of view.

Three sizes of valve have so far been produced, with bore diameters of 16 in., 24 in., and 30 in., respectively. Cast in carbon steel, the valve bodies are moulded in three sections. Submerged arc welding is used to join the main body castings, which are required to withstand pressures up to 2,400 lb./sq. in. Non-destructive tests are applied to the valve body castings, and the welded joints are tested by radiographic inspection. Largest of the assembled valves is approximately 10 ft. high and weighs more than 8 tons.

## Personal News

METROPOLITAN-VICKERS ELECTRICAL CO., LTD., have recently announced a number of new appointments. MR. C. H. FLURSCHEIM, Chief Electrical Engineer, has been appointed a Director of the Company; Mr. L. H. J. PHILLIPS has been appointed Assistant Commercial Manager, and is succeeded as Sales Manager, Electronics Department, by Mr. A. G. BARTON; Mr. N. R. D. GURNEY, formerly Chief Engineer, Electrical General Engineering Department, has been appointed Sales Manager, Plant Department, in succession to Mr. R. J. COCHRAN who is seconded to special duties; Mr. Gurney is succeeded by Mr. O. T. EVANS.

MR. F. MOORE has been appointed Deputy Chief Engineer of Steel, Peech and Tozer, a Branch of The United Steel Cos., Ltd. Mr. Moore joined the Appleby-Frodingham Branch in 1922, has been at Steel, Peech and Tozer since 1946, where he was Assistant Mechanical Maintenance Superintendent until his new appointment.

MR. S. G. P. DE LANGE has relinquished his responsibilities as Commercial Manager of the Industrial Products Division of Philips Electrical, Ltd., and in view of his long experience, has been appointed advisor to the company and co-ordinator in all matters affecting industrial products. He is succeeded as Commercial Manager by Mr. C. W. V. DAVIS, at present Manager of the Filtration Department.

DR. E. G. WEST has been appointed Chairman of the Research Board of the British Welding Research Association, consequent upon the resignation from that position of PROFESSOR G. WESLEY AUSTIN. Dr. West, who is a Fellow of the Institution of Metallurgists and Technical Director of the Aluminium Development Association, left on April 22nd for an extensive tour of Canada and the U.S.A., during which he is to visit the principal aluminium producers and fabricators.

MR. GEORGE BOEX, a former Managing Director, retires from the Board of the British Aluminium Co., Ltd., by rotation on May 6th, 1958. Owing to advancing years he does not wish to seek re-election, but he will continue in a consultative capacity.

THE following appointments are announced by the Cambridge Instrument Co., Ltd.—MR. L. F. COOKE, formerly Head of the Industrial Sales Department, as Commercial Sales Manager; MR. A. T. JONES as Sales Manager of the Mechanical Thermometer Division; and MR. S. A. BERGEN, M.B.E., as Chief Development Engineer.

MR. F. P. LIEBERT has been appointed Works Manager of The English Electric Company's Rugby and Whetstone (Leicester) Establishments, responsible to the General Manager, Rugby and Whetstone, MR. E. M. PRICE.

MR. A. H. GOODGER, who has been Head of the Metallurgical Department of the National Boiler and General Insurance Co., Ltd., for many years, formally retired from full-time service on April 12th, 1958. Among his future activities, Mr. Goodger is being retained in the capacity of Consultant Metallurgist by Messrs. Kennedy & Donkin, the well known consulting engineers in the electrical generation and transmission fields.

MR. T. G. GIBSON has been appointed Stud Welding Sales Engineer for Scotland, N. Ireland and Eire, by Crompton Parkinson (Stud Welding), Ltd.



# RECENT DEVELOPMENTS

## MATERIALS : PROCESSES : EQUIPMENT

### Combustion Additive for Solid Fuels

CONSIDERABLE advantages are claimed for the use of a new combustion additive—Amber SSR. 115. This new addition to the range of the Amber Chemical Co., Ltd., is a fine powder for use with solid fuel, and is similar to its companion product, Amber SSR. 113 (for use with residual fuel oil). Amber SSR. 115 has been used in a four-week full-scale trial on the seven Babcock & Wilcox boilers (chain grate stokers) that emit from one stack in a large steam-raising installation in the North-West of England. It was fed direct into the combustion zone through the Amber patented injection system, two injectors per boiler, at the standard dosage rate of 2 lb./ton of fuel burnt.

The results showed that product SSR. 115 can achieve on the treatment of solid fuels similar results to those achieved by Amber SSR. 113 for the treatment of heavy residual fuel oils. These may be summarised as under:—

- (i) Reduction of sulphur corrosion and of the build-up of deposits.
- (ii) Improvement in heat transfer, and therefore efficiency of operation, with its attendant reduction in fuel consumption.
- (iii) A considerable extension of the period that boilers can remain in operation before being shut down for cleaning.
- (iv) Reduction in total stack emission and in its acidic nature.

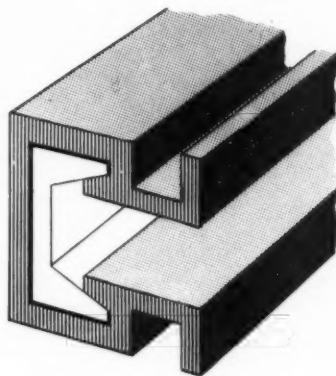
Based on the dosage of approximately 2 lb./ton of fuel (standard for products SSR. 113 and SSR. 115), cost of treatment works out at approximately 1/6d. per ton of fuel burnt.

Amber Chemical Co., Ltd., 11a Albemarle Street, London, W.1.

### Safety Shield for Exposed Conductors

A NEW type of fully-insulated conductor, designed to prevent the possibility of shocks through accidental physical contact, has been introduced by British Mono-Rail, Ltd., for use on all types of overhead handling systems normally using exposed conductor bar electrification. The conductor or bus bar is a straight or curved length of channel section— $\frac{3}{4}$  in. wide,  $\frac{3}{8}$  in. deep, and  $\frac{1}{2}$  in. thick—made of corrosion-resistant electro-galvanised steel enclosed in an extruded red P.V.C. sleeve of special design. The shielding is claimed to be fool-proof in use—even a man's little finger cannot be inserted to make contact—but the efficient functioning of the sliding shoe connector is not impaired. The grade of P.V.C. being used has a high dielectric strength, outstanding resistance to a wide range of chemicals, and high physical strength. A number of accessories have also been introduced, including P.V.C. safety covers, with provision for power feed, which clip over splices in the conductor bars; neoprene caps which fit over the shielding to protect the ends of a system, and insulating sections for use where conductor bars must be isolated.

The system, which is known as Kant-Shock, eliminates



all risk of accidents, so that many overhead handling systems now operating on 50 V. can change over with safety to higher working voltages, with obvious economies. British MonoRail will offer the Kant-Shock shielded conductor for use with their own automatic transfer and overhead handling system, but it will also be available for use with other electrified systems using the standard sized channel section. On an extensive installation, it is estimated that the Kant-Shock system, including bus bars and collectors, would be considerably cheaper than installing sheet steel shielding alone.

British MonoRail, Ltd., Wren Works, Chadderton, Lancs

### Transformer Plug

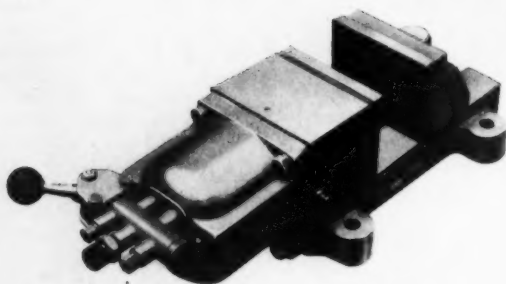
A NEW device—the Dohm Electran transformer plug, has been introduced for the safety of operatives working with long lead electrical appliances. Robustly constructed and cased in hard oil-resisting rubber, it is so compact that it is almost as small as an ordinary plug. It is plugged into a 3-pin socket, direct to the existing mains supply, and steps down the voltage from 240 to 25, which is suitable for low-voltage inspection lamps, soldering irons, machine tools, etc.

One of the hazards of industry is trailing cable, used with portable electrical appliances. A frayed lead, a defective connection, a breakdown in insulation, or even a wet floor, can all lead to fatal accidents. Previously, the only safeguard has been either to install a costly low voltage wiring system, or to use expensive and cumbersome transformer units (where the lead between the transformer unit and the power point remains as dangerous as before). The new transformer plug gives safety and mobility for equipment rated at 40 watts or less, at a comparatively low cost.

The Dohm Group, 167 Victoria Street, London, S.W.1.

### Pneumatic Bench Vice

A SAFETY cover, totally enclosing the distance travelled by the moving jaw of their pneumatic bench vice, has been incorporated by the Consolidated Pneumatic Tool Company, in the latest version of this unit. Substantial saving of time and labour can be achieved by the use of



this tool in operations where many changes of working position are necessary, requiring frequent operation of the vice jaws. This time saving aspect is effected by the simple air control provided, which opens or closes the jaws in a fraction of the time taken by manually operated vices. Particular applications are those of fettling and polishing, component assembly and many forms of repair work.

The vice incorporates a 4 in. diameter air cylinder which gives 1,000 lb. pressure when operating on an 80 lb./sq. in. line pressure. The stroke of the piston and the moving jaw which it actuates is 1 in. whilst the rear vice jaw is adjustable by means of a locating nut to allow work from  $\frac{1}{16}$  in. to 5 in. in size to be accommodated. Jaw size is  $3\frac{5}{8}$  in. by  $4\frac{1}{2}$  in. The unit is housed in a cast iron base, the jaws being of machined steel. Air control is by a double acting hand valve, although a foot control may also be supplied.

*The Consolidated Pneumatic Tool Co., Ltd., 232, Dawes Road, London, S.W.6.*

### Millivoltmeter Controllers

HONEYWELL-BROWN, LTD., announce the availability of indicating millivoltmeter controllers. Being relatively inexpensive, they enable automation to be applied to simpler processes, and are ideal for secondary policing and alarm functions on big installations. Two ranges of millivoltmeter instrument, the Pyr-O-Vane and Protect-O-Vane, provide between them a wide choice of control forms for temperature, etc.

Accuracy of all models is  $\pm 3\%$  of scale span, with dual compensation for ambient conditions. The high-resistance circuit makes accuracy independent of long leads, giving versatility of mounting location. Control forms available on the Pyr-O-Vane controller include on-off, 2- and 3-zone, and time-proportioning action: neutral zones for 3-position control are adjustable. The Protect-O-Vane model has been specially developed to shut the process down or give an alarm signal when temperature exceeds the set-point. Sensitive vane-type control on all models ensures reliable snap-action at set-point.

Plug-in design of measuring and control units facilitates inspection, maintenance and change-over of range and control action. A universal-mounting case houses both measuring and control units in separate compartments. Fail-safe action includes automatic shut-down on power or component failure. Thermocouple burn-out protection is an optional feature.

Further details of both types of millivoltmeter are given in Specification Sheet S103-1 (Pyr-O-Vane Models) and Specification Sheet S103-2 (Protect-O-Vane Models).

*Honeywell-Brown, Ltd., 1 Wadsworth Road, Perivale, Greenford, Middlesex.*

### Hard-Facing Powder

A NEW nickel-base hard-facing powder, \*Colmonoy No. 75, containing tungsten carbide and chromium borides, is recommended for use with the \*Sprayweld process in applications requiring exceptional resistance to abrasion or to combined abrasion and galling. The tungsten carbide makes it especially well suited to applications involving wear caused by scrubbing action or metal-to-metal contact.

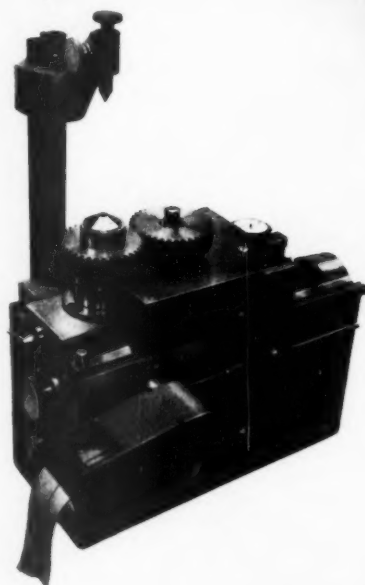
Since Colmonoy No. 75 is suitable for Sprayweld application, part shape is no limitation. It provides significant economies, particularly in applications involving cylindrical parts. Shaft sleeves, pump components, bushings, buffing fixtures, steady-rest jaws and chip-breakers for cutting tools are typical of applications where service life can be lengthened and replacement and maintenance costs reduced. Colmonoy No. 75 is not recommended, however, for elevated temperature applications where high oxidation resistance is a prime consideration.

\* Registered trade mark.

*Wall Colmonoy Corporation, 19345 John R. Street, Detroit 3, Michigan, U.S.A.*

### Gear Roll Tester

THE new David Brown No. 9R gear roll testing instrument provides a simple, rapid and positive means of checking concentricity, tooth contact, centre distance and tooth thickness of a wide range of gears. The standard instrument accommodates spur and helical gears up to 9 in. centres, while precise fitting and easily



interchangeable attachments are available for shaft gears, bevel gears and worm gears. Gears undergoing test are driven by a variable speed motor, the same power unit driving the recording head which automatically gives a full and permanent graph.

Errors are shown on a dial indicator which is in contact with a sensitive carriage loaded by adjustable spring pressure. The dial is graduated to 0.0005 in. as standard, but 0.0001 in. graduation can be provided if required. Actual gear centre distances are read directly from the vernier scale at the front of the instrument. The graphic recorder gives a magnification of 250 to 1, and the drive is arranged so that one revolution of the gear under test produces a graphical recording 12 in. long. The variable speed motor allows the gear speed to range from  $\frac{3}{4}$  to 2 r.p.m., the feed mechanism ensuring a positive relationship between gear and graph paper.

The standard instrument accommodates spur and helical gears, but an attachment for shaft gears is available, consisting of a vee-section pillar, located on the bed and carrying an adjustable top centre (this is shown fitted in the accompanying picture). Units for bevel and worm gears are separately mounted on the sensitive carriage.

With this instrument backlash in a pair of gears can be calculated by noting the difference between the working centre distance and the centre distance when the gears are in metal-to-metal contact.

David Brown Industries, Ltd., Tool Division, Huddersfield.

### pH Meter Test Set

THE Lock universal pH meter test set is a simple well-made instrument for quickly checking and localising faults on pH meters and on pH electrode systems, and for assisting in the checking and setting up of industrial pH measuring, recording and control gear. It consists basically of a long-life dry cell across which is connected a number of high stability resistors forming a potentiometer. These resistors connect to a multi-position selector switch which selects an increasing number of millivolts as it is rotated in a clockwise direction, each step approximating to 2 pH units. A number of interconnecting leads are provided for connecting to the pH meter under test. Two output connections to the pH meter are provided, a low impedance one, and a high impedance one of approximately 250 megohms, to simulate the high resistance of normal glass electrodes.

No electrical knowledge is required to make full use of this instrument; full operating instructions, together with some general information on the use and care of pH electrodes are provided with each test set. A carrying case is available if required.

A. M. Lock & Co., Ltd., 79 Union Street, Oldham, Lancs.

### Shielded Inert Gas Welding Equipment

QUASI-ARC have developed new semi-automatic equipment for shielded inert gas metal-arc welding. Known as the Lynx, the equipment has many new features, prominent among which are the following:

- (a) A welding rectifier which is self-contained, having control of all the services required for the process—welding current, wire feed, gas flow and water cooling.



- (b) A light and portable wire feed and control unit which the welder, unaided, can readily re-position around large fabrications, and which he can easily part into two assemblies for carrying over longer distances.
- (c) Motorized remote wire feed speed control.
- (d) A choice of water-cooled or air-cooled guns which are readily interchangeable without any modification of the equipment.

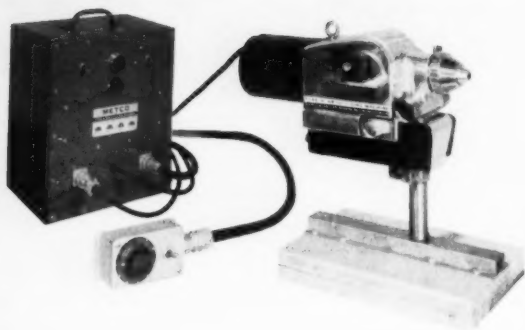
The Lynx equipment is designed for welding aluminium and its alloys, copper and its alloys, corrosion-resisting steels, mild steel, etc. Welding speeds are high; in aluminium, using  $\frac{1}{8}$  in. wire at a current of 245 amp., a  $\frac{1}{4}$  in. horizontal-vertical fillet weld can be deposited at an overall welding speed of 18 in./min. The same size of weld is deposited at 15 in./min. on corrosion-resisting steels and mild-steel. Welding is continuous as there is no pause to change electrodes and there is no slag to remove. The Lynx can be used for welding all metals greater than  $\frac{1}{8}$  in. thick.

Quasi-Arc, Ltd., Bilston, Staffs.

### Metal Spraying Machine

A NEW metal spraying gun, equally suited for use as an individual unit, or as an integral part of a large production set-up, has been introduced by Metallizing Equipment Co., Ltd. The new unit, known as the Metco Type K Metallizing Machine, meets the current trend towards high-speed, semi-automatic, production metal spraying. The many uses for this type of equipment include hard-facing the friction surface of heavy-duty clutch pressure plates; spraying wear-resistant liners into aluminium cylinder blocks; building-up large hydraulic rams, rolls, shafts, etc., with stainless steel; production salvage of mis-machined parts; and high-speed deposition of zinc and aluminium for corrosion prevention.

In operation, the gas-head employs the same basic principles as existing Metco metallizing equipment: the



metal to be sprayed is in wire form, and is heated by an oxygen-gas flame. The wire feed of the Type K machine is driven by a high capacity electric motor, monitored by an electronic speed control system permitting adjustment of wire speed through the entire usable range. The power supply unit maintains constant wire speed, and automatically compensates for all the usual variations in line voltage: it operates from a single phase supply of 110-250 V. A.C. The controls provide high-speed acceleration and dynamic braking for instantly starting or stopping the wire feed during use, which, together with the speed control, can be operated by a remote unit. The motor, gearbox and control unit are totally enclosed and sealed to prevent ingress of metallic dust. All rotating parts run on ball bearings and the gears are sealed in gear oil which is pumped to provide positive lubrication in all operating positions. The construction of the gun is such that the unit should not need to be taken out of service for overhaul more frequently than once a year or at 2,000 hour intervals.

*Metallizing Equipment Co., Ltd., Chobham, Woking, Surrey.*

### Bromide Sodium Safelamp

THE Kodak bromide sodium safelamp has been specially developed to provide a very high level of "safe," suitably filtered and diffused orange-red illumination, where Kodak Bromesko and bromide papers or Statfile papers are handled. The combination of sodium light with filtered tungsten prevents the "livid" effect of sodium lighting alone and gives pleasant working conditions. The illumination is such that it is possible to judge print quality and read labels in comfort and without eyestrain as far away as 14 ft. from the lamp. Other features of the safelamp include a remarkably long working life of some 4,000 hours of continuous running, with very low running costs. Light from one safelamp consumes only 75 watts, and yet will illuminate an area which would require ten normal safelamps consuming 250 watts.

The lamp is cylindrical in shape and has an outer case sturdily moulded from red Perspex material, the two end pieces being black Perspex mouldings. One of these is fitted with two B.C. lampholders to accommodate a 45 watt sodium lamp and a 15 watt tungsten lamp. The other end is fitted with a single B.C. lampholder for a 15 watt tungsten lamp. Two chains are supplied with the lamp to suspend it from the ceiling. A ceiling block

into which the electrical connections from the safelamp are plugged, a special transformer and a P.F. capacitor for the operation of the sodium lamp are also supplied.

*Kodak, Ltd., Kingsway, London, W.C.2.*

### Diaphragm Valves for Process Control

HONEYWELL-BROWN, LTD., are now making a comprehensive range of diaphragm control valves, complementing their established range of miniature and conventional pneumatic controllers. Single-seated, double-seated, low-flow and three-way types are all available on short delivery in a variety of body and trim materials.

Single-seated valves give throttling action with tight shut-off, and a choice of plug types provides equal percentage, linear or quick-opening action: sizes range from 1 in. to 8 in. Double-seated valves, for pressure-balanced throttling action on processes where fluid pressure is high, offer the same range of plug types, with the addition that equal percentage plugs can be either V-ported or contoured: sizes range from 1 in. to 8 in. Low-flow valves are available in body sizes from  $\frac{1}{8}$  in. to 1 in. Reduced port sizes ranging from  $\frac{1}{8}$  in. to  $\frac{3}{4}$  in. give flow coefficients suitable for low flow control, both in the laboratory and in process work: plug action is equal percentage. Three-way valves, single—and double-seated, can be piped for mixing or diverting service. Design ensures that flow always tends to open the plug, gives increased stability and eliminates slamming: body sizes range from  $\frac{1}{8}$  in. to 8 in. All control valves are available in cast iron, cast steel or stainless steel. Cast iron valves are supplied with bronze trim: cast steel or stainless steel types normally have hardened steel trim, but Stellite or Monel trim can also be furnished.

*Honeywell-Brown, Ltd., 1 Wadsworth Road, Perivale, Middlesex.*

### Electrode Improvement

MODIFICATIONS which will bring about an improvement in the performance of the low-hydrogen type of electrode are announced by Quasi-Arc, Ltd. The high weld metal quality given by these electrodes is dependent to a large extent on the formation of a gas shield round the arc. In the short period of time which elapses after striking the arc and before the gas shield has formed, porosity may occur. To eliminate this problem, a paste of special composition has been developed which can be applied to the tip of the electrodes after the normal coating has been extruded on the core wire. The tip is designed to generate shielding gases as soon as possible after the arc is struck. The welder can now deposit a bead without the necessity of "running back" over the start of the weld to eliminate porosity. Arc striking is easier, since repeated tapping or scratching is no longer necessary, and the arc strikes as soon as the electrode is applied to the workpiece.

The tip is now being applied to the Quasi-Arc Ferromax electrode—an iron powder type which, although it has a rutile-type coating, gives a low-hydrogen deposit. The advantages in speed of welding, quality of deposit and high weld metal recovery rate conferred by the iron powder and by the special design of the coating have now been increased by the addition of the tip.

*Quasi-Arc, Ltd., Bilston, Staffs.*



# LABORATORY METHODS

MECHANICAL • CHEMICAL • PHYSICAL • METALLOGRAPHIC

INSTRUMENTS AND MATERIALS

MAY, 1958.

Vol. LVII, No. 343

## Composite Procedure for the Determination of Mo, Ni, Mn, Fe, Cr, Sn, V and N in Titanium Alloys

By George Norwitz and Maurice Codell

*Pitman-Dunn Laboratories, Frankford Arsenal, Philadelphia, Pa., U.S.A.*

*A composite procedure is proposed for the determination of eight elements in titanium alloys. Molybdenum is determined colorimetrically with thiocyanate or gravimetrically or volumetrically after a sulphide precipitation. Nickel is determined colorimetrically or gravimetrically with dimethylglyoxime. Manganese is determined by the periodate colorimetric method, or by titration with arsenite. Iron is determined colorimetrically with ortho-phenanthroline, or by titration with dichromate. Chromium is determined colorimetrically with diphenylcarbazide, or by titration with ferrous sulphate. Tin is determined iodometrically. Vanadium is determined by titration with ferrous sulphate, using sodium diphenylbenzidine sulphate indicator. Nitrogen is determined volumetrically after distillation.*

UNDER a programme sponsored by the Wright Air Development Centre, the Pitman-Dunn Laboratories were requested to develop a composite procedure for the analysis of titanium alloys, whereby several elements are determined on aliquots taken from a "master solution." The advantages of such a procedure are considerable savings in time, chemicals and glassware. Composite procedures are frequently used in the analysis of many types of metals and alloys, but none has been proposed for titanium alloys. Thompson<sup>38</sup> has described a composite procedure for determining manganese, iron, magnesium, and nitrogen in sponge titanium, but the problems encountered with relatively pure titanium are somewhat different from those with titanium alloys.

### Preparation of Master Solution

In developing a sequence procedure for titanium alloys, the best method found for dissolving the sample was by means of a mixture of moderately dilute sulphuric acid and a little hydrofluoric acid. The titanium was then oxidized with hydrogen peroxide and the solution evaporated to fumes of sulphuric acid. In this treatment the silicon is volatilized as silicon tetrafluoride and the boron as boron trifluoride. Up to 4% tungsten can be held in solution because of the solvent action of titanium on tungstic acid. If more than this amount of tungsten is present, the small amount of precipitate that remains undissolved is easily filtered off. Attempts to prepare a master solution by dissolving the sample in hydrofluoric acid, followed by addition of boric acid to complex the fluoride, were unsuccessful. The reaction with hydrofluoric acid was too vigorous to control when a 5 or 10 g. sample was used, and a heavy precipitate (probably titanium fluoborate) was sometimes obtained on addition of sufficient boric acid to complex the fluoride ion.

### Molybdenum

Having decided on a master solution containing sulphuric acid, the next step was to establish conditions for

the determination of molybdenum on an aliquot. Vigo<sup>23, 39</sup> has proposed a colorimetric method for determining molybdenum in titanium alloys by the thiocyanate method, using a perchloric acid medium. In this method a 0.5 g. sample is dissolved in hydrofluoric acid, and an aliquot containing 0.05 g. of sample evaporated to fumes of perchloric acid. Ferric perchlorate solution is then added, followed by a mixture of thiocyanate and stannous chloride. The addition of acetone or other water-soluble solvent to stabilize the colour is not necessary. Vigo's method has been shown to be very accurate, but care must be taken to avoid precipitation of metatitanic acid when the sample is fumed with perchloric acid. Furthermore, more than 0.5% tungsten or tin may interfere, because of hydrolysis during the fuming with perchloric acid.<sup>23, 39</sup>

It was found that the molybdenum thiocyanate colorimetric method was applicable to an aliquot of the master solution if perchloric acid and ferric perchlorate were added. The optimum amount of acid for the 100 ml. volume, in which the colour was developed was approximately 0.25 to 0.5 ml. sulphuric acid and 10 ml. perchloric acid (60%). Much variation from this acidity caused the colour to fade. It was not necessary to add acetone or other water-soluble solvent to stabilize the colour. The reason for the stability of the colour is the presence of the perchloric acid<sup>29</sup> and iron.<sup>6, 24, 37</sup> The iron also increases the intensity of the colour, the maximum effect being reached when 1 or 2 mg. of iron are present.<sup>6, 24, 37</sup> When moderate amounts of molybdenum were present, the molybdenum colour developed completely in 5 minutes. However, when relatively small amounts of molybdenum (about 0.1%) were present, complete colour development required 15 minutes, because of a repressive action of the 0.05 g. of titanium. No colour at all could be developed for samples containing less than 0.05% molybdenum. Solutions containing no titanium gave immediate development of as little as 0.01% molybdenum.

TABLE I.—COLORIMETRIC RESULTS FOR MOLYBDENUM IN THE PRESENCE OF POSSIBLE INTERFERENCES.

Molybdenum Present (%)	Other Elements Present (%)	Molybdenum Found (%)
0.60	10 Al	0.61
0.60	10 Mn	0.59
0.60	10 Sn	0.61
0.60	10 Fe	0.60
0.00	10 Cr	0.00
0.60	10 Cr	0.59
0.00	10 Ni	0.005
0.60	10 Ni	0.60
0.00	5 W	0.04
0.00	3 W	0.015
0.00	1 W	0.005
0.60	5 W	0.63
0.60	3 W	0.61
0.60	1 W	0.60
0.00	7.5 V	0.01
0.00	5 V	0.00
0.00	2.5 V	0.00
0.60	7.5 V	0.61
0.60	5 V	0.59
0.60	2.5 V	0.59
0.00	10 Co	0.01
0.00	5 Co	0.00
0.60	10 Co	0.61
0.60	5 Co	0.60
0.00	2.5 Cu*	0.00
0.00	1 Cu*	0.00
0.60	2.5 Cu*	0.54
0.60	1 Cu*	0.58
0.60	0.25 Cu	0.60

\* CuUNS filtered off.

A study was made of the interferences with a colorimetric method for molybdenum. The results are summarized in Table I. The following did not interfere up to concentrations of 10%: aluminium, manganese, tin, iron, chromium and nickel. More than 2% tungsten, or 7.5% vanadium interfered slightly because of the formation of yellow and yellowish-green colours, respectively, and 10% cobalt interfered very slightly because of the formation of a faint bluish colour. The interference from cobalt would be larger if acetone or other water-soluble solvent were added. More than 0.25% copper interfered because of partial precipitation of cuprous thiocyanate. By filtering off the cuprous thiocyanate, up to 1% copper could be tolerated. If more than 1% copper were present, the results for molybdenum were low, presumably because of the consumption of thiocyanate in precipitating the copper. Copper is not an important alloying element in titanium alloys.

It is important to use high purity stannous chloride in developing the molybdenum thiocyanate colour. Some lots of stannous chloride when dissolved in hydrochloric acid give a distinct odour of hydrogen sulphide. The use of such stannous chloride will cause the colour to fade.

The maximum range suggested for the colorimetric method for molybdenum is approximately 3%. Amounts of molybdenum greater than this can be determined by adding hydrofluoric and tartaric acids to an aliquot of the master solution, precipitating the molybdenum as the sulphide and igniting to the oxide.<sup>25</sup> If copper and tin are present, the sulphide precipitate is dissolved by fuming with sulphuric acid, and after dilution the copper and tin are removed by the addition of metallic zinc.<sup>3, 23</sup> The solution is then passed through a Jones reductor and titrated with permanganate.<sup>3, 23</sup>

### Nickel

Up to 3% nickel in titanium alloys can be determined colorimetrically. Amounts of nickel greater than 3% are

best determined gravimetrically. Tour<sup>39</sup> and Corbett<sup>40</sup> have indicated that the dimethylglyoxime colorimetric method is applicable to titanium alloys. In the present paper a complete study is made of the colorimetric determination of nickel in titanium, using iodine as the oxidizing agent. Haywood and Wood,<sup>16</sup> Cooper,<sup>8, 9</sup> and Haim and Tarrant<sup>14</sup> have used iodine for the colorimetric determination of nickel in steels, aluminium alloys and copper-base alloys. In determining nickel in titanium, the following reagents are added to a 0.05 g. aliquot of the master solution: ammonium citrate solution, iodine solution (0.02 N), ammonium hydroxide, and dimethylglyoxime. The colorimetric readings should be made within 10 minutes. After 10 minutes the colour of the solutions increases steadily for about 4 hours and then gradually decreases. This effect for three typical concentrations of nickel is shown in Table II. Titanium had no effect on the nickel dimethylglyoxime colour, and as little as 0.02% nickel could readily be determined on an aliquot containing 0.05 g. sample. Several experiments indicated that trace amounts of nickel could be determined by taking an aliquot containing 0.25 g. sample and then adding 15 ml. of ammonium citrate solution and a 5 ml. excess of ammonium hydroxide (1 to 1).

A study was made of the possible interference from elements that might be found in titanium alloys. The results are summarized in Table III. The following did not interfere when present in concentrations up to 10%: aluminium, tin, vanadium, tungsten and molybdenum. More than 7.5% iron interfered slightly because of the yellow colour of the ferric citrate ion. More than 5% chromium interfered somewhat because of the green colour of the chromic citrate ion. The interferences from iron and chromium can be corrected for by using a blank sample to which everything but the dimethylglyoxime is added. Manganese does not interfere significantly with the method when present to the extent of less than 2.5%. When 2.5–7.5% manganese is present, the result for nickel will be about 0.02 to 0.05% too high because of the yellow colour of the manganese citrate complex. When more than 7.5% manganese is present, low results will be obtained for nickel because the iodine is consumed in oxidizing the manganese. Because of the lack of iodine, some of the nickel will be precipitated as nickel dimethylglyoxime. When bromine water was used in place of iodine solution similar interferences from manganese was encountered. When ammonium tartrate was used in place of the ammonium citrate, the interference from manganese was slightly greater because the colour of the manganic tartrate complex is yellowish brown. If no citrate or tartrate were present, the manganese would interfere because of the formation of a brown precipitate of manganese dioxide. The interference of 2.5–7.5% manganese is easily corrected for by carrying along a blank sample. The interference of more than 7.5% manganese can be corrected for by adding excess iodine solution (10 ml.) and carrying along

TABLE II.—EFFECT OF TIME ON COLORIMETRIC READINGS FOR NICKEL.

Nickel Present (%)	Percent Transmittance After									
	5 min.	10 min.	20 min.	30 min.	1 hr.	1.5 hr.	2 hr.	4 hr.	6 hr.	7.5 hr.
0.2	78.2	78.2	77.9	77.5	77.3	77.4	77.1	75.8	80.5	81.3
0.6	48.3	48.2	46.9	44.2	41.1	41.1	40.2	37.2	41.8	42.2
1.2	23.5	23.5	22.2	20.0	18.2	16.2	16.0	13.3	17.2	17.4

a blank sample. Less than 1% cobalt does not interfere significantly with the method. When 1-5% cobalt is present, the result for nickel will be about 0.02-0.06% high due to the formation of a yellowish cobalt dimethylglyoxime complex. A fairly good result can be obtained for alloys containing more than 1% cobalt by carrying along a blank sample. There is no significant interference from less than 0.5% copper. When more than this amount of copper is present, high or low results will be obtained depending upon the amount of nickel present. The tendency towards high results is caused by the formation of a purple copper dimethylglyoxime complex. The tendency towards low results is caused by the consumption of the dimethylglyoxime in the formation of this complex. Attempts to correct for the interference of copper by adding an excess of dimethylglyoxime and carrying a blank sample were unsuccessful. One reason for the failure was the fading of the colour of the copper dimethylglyoxime complex.

Apparently, previous investigators have not worked out the conditions for the direct gravimetric determination of nickel in titanium alloys with dimethylglyoxime. Baird and Miles<sup>5</sup> precipitated nickel in titanium alloys with dimethylglyoxime after a prior ammoniacal separation of the titanium, while Corbett<sup>11</sup> recommended a prior sulphide separation of the nickel from an alkaline citrate medium. In order to determine nickel directly in titanium alloys, it was found necessary to use a large excess of citric acid to hold the titanium in solution. Also, the nickel dimethylglyoxime precipitate should be washed with ammoniacal ammonium citrate solution to prevent possible hydrolysis of the titanium while washing. The danger of co-precipitating titanium with the nickel

TABLE IV.—GRAVIMETRIC RESULTS FOR NICKEL IN THE PRESENCE OF POSSIBLE INTERFERENCES.

Nickel Present %	Other Elements Present %	Nickel Found %
1.60	10 Mn	0.98
2.00	10 Mn	1.99
1.50	10 Cu	1.43
1.50	7.5 Cu	1.46
1.50	5 Cu	1.49
1.50	2 Co	1.85
1.50	1 Co	1.62
1.50	0.5 Co	1.53

precipitate is most apparent for larger amounts of nickel, there being little danger of co-precipitation when less than 0.3% nickel is present. When more than 0.3% nickel is present the solutions should be filtered hot after digesting at 70-80° C. for 30-60 minutes. For the determination of 0.03-0.1% nickel it is necessary that the solution be allowed to stand overnight at room temperature to obtain complete precipitation. Tartaric acid should not be used in place of citric acid, since tartaric acid will not prevent some co-precipitation of titanium when larger amounts of nickel are being determined.

The only elements that might interfere with the gravimetric determination of nickel in titanium alloys are copper, cobalt, and possibly manganese.<sup>22, 30</sup> The results obtained for the method in the presence of copper, cobalt and manganese are shown in Table IV. 10% manganese did not interfere at all. Up to 5% copper did not interfere, but when more than 5% copper was present the results for nickel were somewhat low. When copper was present, twice the amount of dimethylglyoxime solution as would customarily be used was added, since dimethylglyoxime is consumed in forming a complex with the copper. The presence of more than 0.5% cobalt, will cause high results. When more than this amount of cobalt is present, it is necessary to redissolve the nickel precipitate in acid and make a re-precipitation.<sup>1, 22</sup> Attempts to eliminate the interference of cobalt by adding hydrogen peroxide or ammonium persulphate to oxidize the cobalt to the trivalent state, followed by a 20-minute boiling period to destroy the excess oxidizing agent,<sup>22</sup> were unsuccessful, low and erratic results being obtained. Other means for determining nickel with dimethylglyoxime when cobalt is present have been suggested, including the use of a buffered acetate medium<sup>7</sup>; prior oxidation of the cobalt with ferricyanide<sup>34</sup>; and prior complexing of the cobalt with cyanide.<sup>13, 19</sup> These methods were not investigated, since titanium alloys containing nickel and more than 0.5% cobalt are extremely rare.

### Manganese

Previous investigators who determined manganese in titanium by the periodate colorimetric method developed the colour in media containing about 15 ml. of sulphuric acid and 20 ml. nitric acid per 100 ml. of solution,<sup>38</sup> and 35 ml. sulphuric acid and 10 ml. nitric acid per 155 ml. of solution.<sup>23</sup> In the present paper, a medium containing 10 ml. of sulphuric acid (no nitric acid) per 80 ml. of solution is used. The use of nitric acid for the colorimetric determination of manganese is not necessary except when ferrous ion, stannous iron or other easily oxidizable ions which would reduce the periodate to iodide are present. In the determination of manganese in steels, an acid mixture containing phosphoric acid is frequently used, the phosphoric acid serving the purpose

TABLE III.—COLORIMETRIC RESULTS FOR NICKEL IN THE PRESENCE OF POSSIBLE INTERFERENCES.

Nickel Present (%)	Other Elements Present (%)	Nickel Found (%)
0.60	10 Al	0.60
0.60	10 Sn	0.60
0.60	10 V	0.60
0.60	10 V	0.59
0.60	10 W	0.60
0.60	10 W	0.60
0.60	10 Mo	0.60
0.60	10 Mo	0.59
0.60	10 Fe	0.615
0.60	7.5 Fe	0.605
0.60	10 Fe	0.62
0.60	7.5 Fe	0.60
0.60	10 Cr	0.64
0.60	7.5 Cr	0.61
0.60	5 Cr	0.605
0.60	10 Cr	0.64
0.60	7.5 Cr	0.62
0.60	5 Cr	0.61
0.60	10 Mn	0.64
0.60	7.5 Mn	0.64
0.60	5 Mn	0.62
0.60	2.5 Mn	0.61
0.60	10 Mn <sup>a</sup>	0.39
0.60	5 Mn	0.63
0.60	2.5 Mn	0.62
0.60	5 Co	0.65
0.60	2 Co	0.62
0.60	1 Co	0.60
0.60	5 Co	0.66
0.60	2 Co	0.64
0.60	1 Co	0.62
0.60	5 Cu	0.10
0.60	2 Cu	0.04
0.60	0.5 Cu	0.91
0.60	5 Cu	0.38
0.60	1 Cu	0.58
0.60	0.5 Cu	0.58

<sup>a</sup> Red precipitate of nickel dimethylglyoxime filtered off.

TABLE V.—COLORIMETRIC RESULTS FOR MANGANESE IN THE PRESENCE OF POSSIBLE INTERFERENCES.

Manganese Present %	Other Elements Present %	Manganese Found %
0.50	10 Al	0.49
0.50	10 Sn	0.50
0.00	10 V	0.00
0.50	10 V	0.50
0.00	10 W	0.00
0.50	10 W	0.50
0.00	10 Fe	0.00
0.50	10 Fe	0.51
0.00	10 Ni	0.00
0.50	10 Ni	0.50
0.00	10 Cu	0.00
0.50	10 Cu	0.50
0.00	10 Co	0.00
0.50	10 Co	0.49
0.00	4 Cr	0.00 Uncorrected
0.00	2 Cr	0.01 Uncorrected
0.00	4 Cr	0.02 Uncorrected
0.00	6 Cr	0.05 Uncorrected
0.00	8 Cr	0.05 Uncorrected
0.00	10 Cr	0.05 Uncorrected
0.50	4 Cr	0.50 Uncorrected
0.50	2 Cr	0.51 Uncorrected
0.50	4 Cr	0.53 Uncorrected
0.50	6 Cr	0.54 Uncorrected
0.50	8 Cr	0.54 Uncorrected
0.50	10 Cr	0.54 Uncorrected
0.00	4 Cr	0.00 Nitrite Method
0.00	8 Cr	0.00 Nitrite Method
0.00	10 Cr	0.00 Nitrite Method
0.50	2 Cr	0.49 Nitrite Method
0.50	4 Cr	0.50 Nitrite Method
0.50	6 Cr	0.50 Nitrite Method
0.50	8 Cr	0.49 Nitrite Method
0.50	10 Cr	0.50 Nitrite Method

of decolorizing the large amount of iron. Phosphoric acid cannot be present in the colorimetric determination of manganese in titanium, because insoluble titanium phosphate would precipitate. It was found that up to 6 mg. of manganese could be readily oxidized in the method described in this paper. In determining larger percentages of manganese it was only necessary, therefore, to dilute to a larger volume after developing the colour, rather than use a smaller aliquot. Titanium has no effect on the manganese colour. By the use of a 50 ml. aliquot, trace amounts of manganese are easily determined.

The effect of interferences with the method are shown in Table V. The following did not interfere when present in concentrations up to 10%: aluminium, tin, vanadium, tungsten, iron, nickel, copper and cobalt. More than 2% chromium interfered somewhat because of the colour of the chromium. This interference is troublesome, because periodate only partially oxidizes the chromic ion to the chromate ion, the amount of oxidation decreasing with increasing acidity.<sup>33</sup> The interference from the bluish-green chromic colour is somewhat greater than the interference from the chromate colour. When more than 2% chromium is present in the sample, the method is modified by adding 5 ml. of 5% urea solution to the permanganate solution before dilution, and then reading the colour, using as a blank a portion of the solution that has been treated with one or two drops of sodium nitrite solution (1%) to bleach out the permanganate colour.<sup>10, 15, 29</sup> The purpose of the urea is to destroy the excess nitrite.<sup>15, 29</sup> The use of the urea is essential for the method described in this paper. If it is omitted, some of the chromate will also be reduced, even in the presence of periodate, causing erroneous results. The effect is easily observed by adding chromate to a titanium sample,

carrying it through the procedure, and observing visually the reduction of the chromate by the nitrite when the urea is not present. Nitrite without urea has been used in the colorimetric determination of manganese in steels.<sup>10</sup> The resistance of the chromate to reduction in that instance may be due to a different acidity, the presence of phosphoric and perchloric acids, or the presence of the large amount of iron. The use of hydrogen peroxide as a bleaching agent<sup>22, 36</sup> in place of the sodium nitrite would not be satisfactory for the determination of manganese in titanium, because the peroxide would react with the titanium to produce a yellow colour. An alternative method to that described above for determining manganese in samples containing several percent chromium, is to oxidize first with silver nitrate and potassium persulphate, and then with periodate.<sup>20</sup> By this means the chromium is completely oxidized to the chromate and the simple correction factor—2% chromium is equivalent to 0.005% manganese—can be applied. A third method for correcting for chromium interference that is applicable to rapid routine work is merely to deduct 0.04% manganese from the result when 4–10% chromium is present in the sample. The validity of this correction lies in the fact that the interference from chromium levels off above 4% chromium to about 0.04%. This is readily seen from the results in Table V. When the permanganate solution is diluted to 500 ml. before reading (instead of 100 ml.), the interference of up to 10% chromium is insignificant. It has been shown that, if the permanganate colour is read at 580 m $\mu$ , there is no interference from chromate at all.<sup>35</sup> However, at this wavelength, the interference from the chromic ion would be greater than at lower wavelengths. By superimposing the transmittance curves of Lingane and Collatt<sup>20</sup> and Kasline and Mellon<sup>18</sup> for manganese, chromate, chromic sulphate (maximum absorption, 580 m $\mu$ ), vanadium, nickel, iron, copper and cobalt, it is seen that, for the method described in this paper, a wave length of 545 m $\mu$  is very satisfactory.

Manganese can be determined in titanium alloys in the range of 0.05–10% by the persulphate oxidation-arsenite titration method. Several milligrams of manganese have been determined in this manner, but it is best to work with a sample containing less than 15 mg.<sup>17</sup> The chromium content of the solution being titrated should not exceed 15 mg.,<sup>17</sup> since the chromate colour obscures the end point. When titrating permanganate with arsenite, the latter reagent should be added rapidly, otherwise some of the manganese will be re-oxidized by the persulphate during the titration.<sup>21</sup> There seems to be a tendency for results by the persulphate oxidation-arsenite reduction method to be somewhat higher than results obtained by the colorimetric method when the manganese content is greater than 3%. This has been confirmed independently by Chase Brass and Copper Company.<sup>39</sup>

#### Iron

Up to 3.7% iron in titanium alloys can be determined colorimetrically on an aliquot of the master solution by the ortho-phenanthroline method. The method has been applied to titanium alloys, using a hydrochloric acid solution<sup>28</sup> and a hydrochloric-fluoboric acid solution.<sup>25</sup> The method is readily applicable to a sulphuric acid solution. Iron in titanium alloys in the range 0.2–10% iron can be determined by titration after a sulphide precipitation of the iron from an alkaline tartrate medium.<sup>23</sup>



## Chromium

Up to 4% chromium can be determined colorimetrically on an aliquot of the master solution, using diphenylcarbazide. This reagent has been used previously for the determination of chromium in titanium alloys in a procedure in which the sample was dissolved in dilute sulphuric acid and the titanium oxidized by the dropwise addition of peroxide.<sup>26</sup> The peroxide was then destroyed and the chromium oxidized by the addition of an excess of permanganate and ammonium persulphate. In the present procedure a large excess of permanganate is not necessary, since there is no peroxide to destroy. An acetone solution of the diphenylcarbazide should be used instead of the ethyl alcohol solution previously recommended.<sup>23, 26</sup> Urone<sup>40</sup> has recently shown that when the diphenylcarbazide reagent is dissolved in high purity acetone the solution will keep for weeks, whereas an alcoholic solution must be made fresh daily. Chromium in the range 0.1–10% chromium can be determined volumetrically on an aliquot of the master solution, after the persulphate oxidation, by titrating with ferrous ammonium sulphate and potassium permanganate in the usual manner.<sup>2, 23</sup>

## Tin

Amounts of tin greater than 0.5% can be determined by treating an aliquot of the master solution with fluoboric acid to complex the titanium and then reducing with iron and titrating with iodine. This is a slight modification of the procedure of Dupraw.<sup>12</sup> From 0.05–10% tin can be determined volumetrically after a sulphide precipitation. The method is a simplified modification of a procedure previously described.<sup>27</sup> In that procedure the titanium was oxidized with permanganate, a step that is unnecessary in the present method.

## Vanadium

Vanadium can be determined on an aliquot by oxidizing with ammonium persulphate and then titrating with ferrous sulphate, using sodium diphenylbenzidine sulphate as an indicator. This is essentially the procedure of Pigott.<sup>23, 31</sup> The presence of hydrofluoric acid is advisable for a sharp end point.<sup>31</sup> Chromium does not interfere.

## Nitrogen

Nitrogen can be determined by adding sodium hydroxide to an aliquot of the sample, distilling in a semi-micro distillation apparatus into boric acid, and titrating with standard alkali.<sup>23, 38</sup>

## Apparatus and Reagents

*Beckman Universal Spectrophotometer (Model B), or Coleman Universal Spectrophotometer (Model 14).*

*Sulphuric Acid (s.g., 1.84).*

*Nitric Acid (s.g., 1.42).*

*Hydrochloric Acid (s.g., 1.18).*

*Hydrofluoric Acid (48%).*

*Fluoboric Acid (48%, Baker and Adamson).*

*Perchloric Acid (70%).*

*Ammonium Hydroxide (s.g., 0.90).*

**Blank Master Solution.**—Dissolve 10 g. of high purity titanium (low manganese and low iron content) in an 800 ml. beaker with a mixture of 200 ml. of water, 90 ml. of sulphuric acid and 2 ml. of hydrofluoric acid. Add an excess of hydrogen peroxide (30%) and evaporate to fumes of sulphuric acid. Add water, cool and dilute to 1 litre.

**Ferric Perchlorate Solution.**—Dissolve 2.5 g. of pure iron (National Bureau of Standards sample 55c.) in a mixture of 40 ml. of water and 40 ml. of perchloric acid (70%). Evaporate to fumes of perchloric acid. While still warm, add 40 ml. of water. Add 400 ml. of perchloric acid (70%) and dilute to 500 ml. with water.

**Stannous Chloride Solution (25%).**—Dissolve 500 g. of high purity  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 400 ml. of hydrochloric acid by warming on the hot plate at 60°C. Cool and dilute to 2 litres with water. Add 5 g. of pure tin metal.

**Thiocyanate-Stannous Chloride Reagent.**—Mix 2 volumes of stannous chloride solution (25%) and 1 volume of sodium thiocyanate solution (10%). Make fresh just before using. Filter if not clear.

**Standard Molybdenum Solution (1 ml. = 0.02 mg. Mo).**—Dissolve 1.500 g. pure molybdenum trioxide in a minimum amount of 15% sodium hydroxide solution and dilute to 1 litre in a volumetric flask. Pipette 20 ml. of this solution into a 1 litre volumetric flask and dilute to the mark.

**Sulphuric Acid-Tartaric Acid-Hydrogen Sulphide Wash Solution.**—Add 15 ml. sulphuric acid and 20 ml. of tartaric acid solution (20%) to 1 litre of water and saturate with hydrogen sulphide.

**Ferric Ammonium Sulphate Solution (10%).**—Dissolve 100 g.  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  in water and dilute to 1 litre.

**Iodine Solution (0.02N).**—Dissolve 2.55 g. iodine and 5 g. potassium iodide in 15 ml. of water and dilute to 1 litre.

**Dimethylglyoxime Solution (1%).**—Dissolve 20 g. dimethylglyoxime in 2 litres of 95% ethyl alcohol by warming on the steam bath.

**Standard Nickel Solution (1 ml. = 0.02 mg. Ni).**—Dissolve 1.0000 g. high purity nickel in 20 ml. nitric acid (1 to 1), cool and dilute to 1 litre in a volumetric flask. Pipette 20 ml. of this solution into a 1 litre volumetric flask and dilute to the mark.

**Ammoniacal Ammonium Citrate Wash Solution.**—Add 25 ml. of citric acid solution (25%) to 1 litre of water, make alkaline to litmus paper with ammonium hydroxide and add about 1 or 2 ml. excess ammonium hydroxide.

**Potassium Periodate Solution (3%).**—Dissolve 30 g. of potassium periodate by boiling with 975 ml. of water and 20 ml. sulphuric acid. Cool and dilute to 1 litre.

**Standard Manganese Solution (1 ml. = 0.05 mg. Mn).**—Dissolve 2.8769 g. potassium permanganate in 200 ml. water and 10 ml. sulphuric acid. Add just enough hydrogen peroxide to reduce the manganese and boil 10 minutes. Cool and dilute to 1 litre in a volumetric flask. Pipette 50 ml. of this solution into a 1 litre volumetric flask and dilute to the mark.

**Sodium Arsenite Solution.**—Dissolve 3.852 g. of  $\text{NaAsO}_2$  in water and dilute to 1 litre.

**Ortho-phenanthroline Solution (0.2 %).**—Dissolve 1 g. of 1, 10 ortho-phenanthroline monohydrate in 500 ml. of water.

**Standard Iron Solution (1 ml. = 0.05 mg. Fe).**—Dissolve 1 g. of pure iron (National Bureau of Standards sample 55 c.) in 100 ml. of hydrochloric acid (1 to 1). Oxidize with hydrogen peroxide and boil a few minutes to destroy the peroxide. Cool and dilute to 1 litre in a volumetric flask. Pipette 50 ml. of this solution into a 1 litre volumetric flask and dilute to the mark.

TABLE VI.—COLORIMETRIC RESULTS FOR MOLYBDENUM IN SYNTHETIC MOLYBDENUM-TITANIUM ALLOYS

Molybdenum Present (%)	Molybdenum Found (%)	Average Molybdenum Found (%)
0.06	0.05 0.04 0.06	0.050
0.10	0.09 0.10 0.10	0.097
0.20	0.21 0.20 0.20	0.203
0.60	0.59 0.59 0.60	0.593
1.20	1.22 1.17 1.18	1.19
2.00	1.97 1.95 2.01	1.98
3.00	3.05 2.98 2.90	2.98

**Ammonium Sulphide Wash Solution**—Add 10 g. tartaric acid and 20 ml. ammonium hydroxide to 1 litre of water, and pass hydrogen sulphide through the solution for 10 minutes.

**Diphenylcarbazide Solution (0.25%)**—Dissolve 0.50 g. of diphenylcarbazide in 200 ml. of *cp* acetone.

**Standard Chromate Solution (1 ml. = 0.01 mg. Cr)**—Dissolve 2.8283 g. potassium dichromate in water and dilute to 1 litre in a volumetric flask. Pipette 20 ml. into a 2 litre volumetric flask and dilute to the mark.

**Standard Chromic Solution (1 ml. = 1 mg. Cr)**—Dissolve 2.8283 g. potassium dichromate in 300 ml. of water. Add 5 ml. of sulphuric acid and 3 g. sodium sulphite. Heat to boiling and boil 15 minutes. Cool and dilute to 1 litre in a volumetric flask.

**Antimony Trichloride Solution (1%)**—Dissolve 5 g. of antimony trichloride in 100 ml. hydrochloric acid and dilute to 500 ml. with water.

**Sulphuric Acid—Hydrogen Sulphide Wash Solution**—Add 10 ml. sulphuric acid to 1 litre of water and saturate with hydrogen sulphide.

**Sodium Diphenylbenzidine Sulphonate Solution (0.001M)**—G. Frederick Smith Chemical Company, Columbus, Ohio.

## RECOMMENDED PROCEDURE

### Preparation of Master Solution

Transfer 5 g. of the sample to a 600 ml. beaker and add 100 ml. of water, 45 ml. of sulphuric acid and 2 ml. of hydrofluoric acid. Allow to stand until the vigorous reaction ceases. Warm gently on the hot plate until the sample has dissolved. Add hydrogen peroxide (30%) until the yellow titanium peroxide complex appears. Put on raised cover glasses and evaporate to fumes of sulphuric acid at moderate heat. Cool and add 300 ml. water. Cool again and dilute to 500 ml. in a volumetric flask. If desired, a 10 g. sample may be dissolved in an 800 ml. beaker with 200 ml. of water, 90 ml. of sulphuric acid and 2 ml. of hydrofluoric acid, and the solution finally diluted to 1 litre.

### Molybdenum

#### Colorimetric (for 0.06–3% Molybdenum)

Pipette an aliquot of the master solution into a 100 ml. volumetric flask. For molybdenum of 0.05–1.2%,

TABLE VII.—COLORIMETRIC RESULTS FOR MOLYBDENUM IN AN ACTUAL MOLYBDENUM-TITANIUM ALLOY (WA 7).

Molybdenum Found by Sulphide Method (%)	Molybdenum Found Colorimetrically (%)	Average % Molybdenum Found Colorimetrically
1.87	1.95 1.88 1.90 1.92 1.95	1.92

use a 5 ml. aliquot, and for molybdenum of 1.2–3% use a 2 ml. aliquot. If a 2 ml. aliquot is used, add 3 ml. of blank master solution. Add 10 ml. of ferric perchlorate solution and dilute to 50 ml. with water. Add 30 ml. of thiocyanate-stannous chloride reagent and swirl. Dilute to the mark with water. In 15 minutes compare with a reagent blank at 460 m $\mu$ . Convert to percentage molybdenum by consulting a calibration curve.

For the preparation of the calibration curve, add 5 ml. portions of blank master solution to 100 ml. volumetric flasks, and add 0, 5, 10, 15, 20, 25 and 30 ml. of standard molybdenum solution. Add 10 ml. of ferric perchlorate solution and proceed as above. Plot percentage transmittance against milligrams of molybdenum.

#### Gravimetric or Volumetric (for 0.5–10% Molybdenum)

Pipette a 100 ml. aliquot into a 400 ml. beaker and add 3 ml. of hydrofluoric acid and 25 ml. tartaric acid solution (20%). Add paper pulp and dilute to 200 ml. with water. Pass a rapid stream of hydrogen sulphide through the solution for 20 minutes. Allow to stand overnight. Filter through a No. 40 Whatman filter paper and wash with sulphuric acid-tartaric acid-hydrogen sulphide wash solution. Char at low heat and ignite at 500° C. for 1 hour. Cool and weigh as molybdenum trioxide. The factor for converting molybdenum trioxide to molybdenum is 0.6667.

If copper or tin is present in the sample, or if it is desired to finish the determination volumetrically, place the washed sulphide precipitate and filter paper into a 250 ml. beaker. Add 10 ml. of sulphuric acid and 10 ml. of nitric acid and evaporate to fumes of sulphuric acid. Add nitric acid dropwise to the fuming solution with a medicine dropper to destroy the organic material. Evaporate to strong fumes. Cool, wash down the sides of the beaker and add a few drops of potassium permanganate solution (3%). Fume again. Dilute to 100 ml. and cool. Add several grams of granulated zinc and swirl for a few minutes. Pass the solution through a Jones reductor, the end of which dips into 30 ml. of ferric ammonium sulphate solution (10%), and titrate with permanganate in the usual manner.<sup>3</sup>

### Nickel

#### Colorimetric (for 0.02–3% Nickel)

Pipette an aliquot of the master solution into a 100 ml. volumetric flask. For 0.02–1.2% nickel, use a 5 ml. aliquot, and for 1.2–3%, use a 2 ml. aliquot. Dilute to 25 ml. with water and add 5 ml. ammonium citrate solution (25%), 5 ml. iodine solution (0.02 N), 10 ml. ammonium hydroxide (1 to 1) and 3 ml. dimethylglyoxime solution (1%). Dilute to the mark and within 10 minutes compare with a reagent blank at 530 m $\mu$ . Convert to percentage nickel by consulting calibration curve.

For the preparation of the calibration curve, transfer 5 ml. portions of blank master solution to 100 ml. volumetric flasks and add 0, 5, 10, 15, 20, 25 and 30 ml. of standard nickel solution. Proceed as above. Plot percentage transmittance against milligrams of nickel.

TABLE VIII.—COLORIMETRIC RESULTS FOR NICKEL IN SYNTHETIC NICKEL-TITANIUM ALLOYS.

Nickel Present (%)	Nickel Found (%)	Average Nickel Found (%)
0.02	0.02 0.03 0.02	0.023
0.10	0.10 0.09 0.09	0.093
0.20	0.20 0.19 0.20	0.20
0.60	0.60 0.60 0.60	0.60
1.20	1.21 1.18 1.22	1.20
2.00	2.01 2.05 1.97	2.01
3.00	3.05 2.96 3.00	3.00

*Gravimetric (for 0.03–10% Nickel)*

Pipette an aliquot of the master solution into a 600 ml. beaker. Use a 100 ml. aliquot for 0.03–2% nickel, a 50 ml. aliquot for 2–4% nickel, and a 25 ml. aliquot for 4–10% nickel. Dilute to 350 ml. and add 30 ml. of citric acid (25%). Add ammonium hydroxide until the solution is alkaline to litmus, and then add 1 or 2 ml. excess ammonium hydroxide. Dilute to 400 ml. and heat to approximately 80° C. Add 0.5 ml. of dimethylglyoxime solution (1%) for each milligram of nickel present, plus 10 ml. in excess. Digest at 70–80° C. for 30–60 minutes. Filter through a tared sintered glass crucible. Police the beaker, and wash the precipitate four times with ammoniacal ammonium citrate solution, heated to about 60–70° C., and four times with water. Dry at 150° C. for 90 minutes, cool and weigh. The factor for converting nickel dimethylglyoxime to nickel is 0.2032.

For nickel contents less than 0.1%, allow the solution to stand overnight at room temperature after adding the dimethylglyoxime.

TABLE IX.—GRAVIMETRIC RESULTS FOR NICKEL IN SYNTHETIC NICKEL-TITANIUM ALLOYS.

Nickel Present (%)	Nickel Found (%)	Average Nickel Found (%)
0.03	0.04 0.03 0.03	0.033
0.10	0.10 0.10	0.100
0.50	0.49 0.50	0.594
1.00	0.99 0.99 0.99	0.99
2.00	1.99 1.98 1.98	1.98
3.00	2.99 2.99 2.98	2.99
10.00	10.00 9.96 9.96	9.97

**Manganese***Colorimetric (for 0.02–6% Manganese)*

Transfer a 10 ml. aliquot of the master solution to a 250 ml. beaker. Add 10 ml. sulphuric acid and dilute to 50 ml. Add 20 ml. of potassium periodate solution (3%). Boil for about a minute and digest just below the boiling point for 15 to 20 minutes. Cool and transfer to a volumetric flask. Use a 100 ml. volumetric flask for 0.02–1.2% manganese, and a 500 ml. volumetric flask for 1.2–6% manganese. If the sample contains more than 2% chromium and less than 1.2% manganese, add 5 ml. of urea solution (5%). Dilute to the mark. Compare colorimetrically with the reagent blank at 545  $\mu$ . If the sample contains more than 2% chromium and less than 1.2% manganese, compare with a portion of the solution to which just enough sodium nitrite solution (1%) has been added dropwise with a medicine dropper to bleach out the permanganate colour. Usually one or two drops of sodium nitrite solution will be sufficient. Convert to percentage manganese by consulting a calibration curve.

For the preparation of the calibration curve, transfer 10 ml. portions of master blank solution to 100 ml. volumetric flasks and add 0, 5, 10, 15, 20, 25 and 30 ml. of standard manganese solution. Add 10 ml. of sulphuric acid and proceed as above. Plot percentage transmittance against milligrams of manganese.

*Volumetric (for 0.05–10% Manganese)*

Transfer an aliquot to a 500 ml. Erlenmeyer flask. For 0.05–1% manganese, use a 100 ml. aliquot, and for samples containing above 1% manganese, use an aliquot

TABLE X.—COLORIMETRIC RESULTS FOR MANGANESE IN SYNTHETIC MANGANESE-TITANIUM ALLOYS.

Manganese Present (%)	Manganese Found (%)	Average Manganese Found (%)
0.02	0.02 0.03 0.02	0.023
0.10	0.09 0.10 0.10	0.097
0.50	0.50 0.50 0.50	0.500
1.20	1.21 1.19 1.18	1.19
2.00	1.99 2.01 2.05	2.02
3.50	3.45 3.47 3.54 3.51 <sup>a</sup> 3.47 <sup>a</sup>	3.49
6.00	6.05 5.95 5.99 5.97 <sup>a</sup> 5.91 <sup>a</sup>	5.97

<sup>a</sup> High purity manganese metal added to titanium.

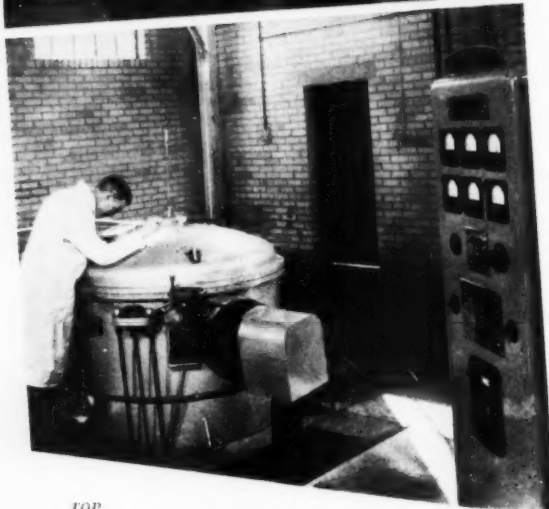
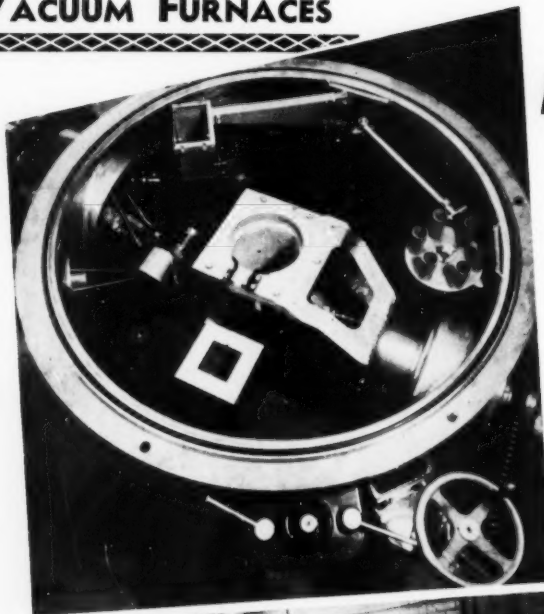
TABLE XI.—COLORIMETRIC RESULTS FOR MANGANESE IN ACTUAL MANGANESE-TITANIUM ALLOYS.

Sample	Manganese Found by Persulphate-Arsenite Method (%)	Manganese Found Colorimetrically (%)	Average Manganese Found Colorimetrically (%)
WA 9	3.55 <sup>a</sup>	3.35 3.29 3.35 3.35 3.41	3.37
WA 10	0.065 <sup>†</sup>	0.06 0.06 0.07 0.07 0.064 (0.5 g. Aliquot) 0.062 (0.5 g. Aliquot)	0.064

<sup>a</sup> Average of results from 4 laboratories.<sup>28</sup>

<sup>†</sup> Average of results from 3 laboratories.<sup>28</sup>

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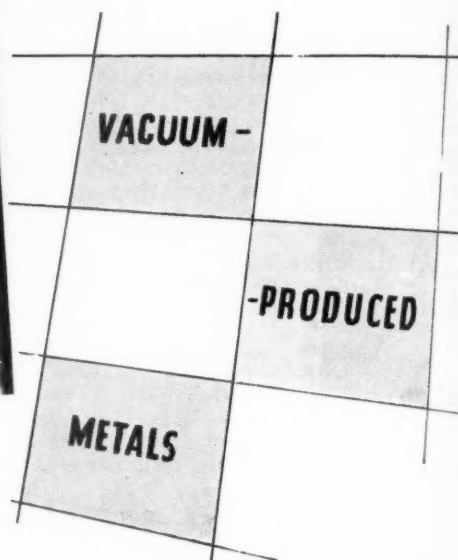
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containing about 10 mg. of manganese. Add sufficient sulphuric acid so that about 10 ml. of concentrated sulphuric acid is present. Add 5 ml. of nitric acid and 8 ml. of silver nitrate solution (1%), and dilute to 150 ml. with water. Heat almost to boiling and add 15 ml. ammonium persulphate solution (25%). Mix well, bring to a boil, and remove from the hot plate immediately. Let stand until the evolution of oxygen ceases (2-3 minutes). Cool to about 20° C. in a running water bath, and add 70 ml. cold water. Titrate rapidly with standard arsenite solution to the disappearance of the pink colour. The arsenite solution is standardized by adding standard manganese solution to aliquots of the blank master solution and carrying the samples through the procedure.

### Iron

#### *Colorimetric (for 0.02-3.7% Iron)*

Pipette an aliquot into a 100 ml. volumetric flask. Use a 5 ml. aliquot for 0.02-0.75%, a 2 ml. aliquot for 0.75-1.8%, and a 1 ml. aliquot for 1.8-3.8%. In measuring a 1 ml. aliquot, use a 1 ml. pipette graduated into tenths. Dilute to 15 ml. with water and add 10 ml. hydroxylamine hydrochloride solution (2%), 5 ml. ammonium tartrate solution (10%), 25 ml. sodium acetate solution (10%), and 10 ml. ortho-phenanthroline solution (0.2%). Dilute to the mark and after 10 minutes compare at 490 m $\mu$  with a reagent blank. Convert to percentage iron by consulting a calibration curve.

For the preparation of the calibration curve, transfer 5 ml. portions of blank master solution to 100 ml. volumetric flasks and add 0, 1, 3, 5, 6, 7 and 8 ml. of standard iron solution. Proceed as above. Plot percentage transmittance against milligrams of iron.

#### *Volumetric (for 0.02-10% Iron)*

Pipette an aliquot into a 600 ml. beaker. Use a 100 ml. aliquot for samples containing less than 2.5% iron, and an aliquot containing about 25 mg. of iron for samples of more than 2.5% of iron. Add 20 g. tartaric acid. Neutralize with ammonium hydroxide and add 10 ml. excess. Pass a rapid stream of hydrogen sulphide through the solution for 20 minutes. Allow to stand for a half hour at 50° C. Filter through a No. 40 Whatman filter paper containing paper pulp, and wash 8 times with ammonium sulphide wash solution. Return the paper and precipitate to the original beaker. Add 50 ml. nitric acid and 15 ml. perchloric acid, and evaporate to strong fumes of perchloric acid. Dilute to 100 ml. with water, neutralize with ammonium hydroxide and add 25 ml. excess. Add 4 g. ammonium persulphate, and boil 5 minutes. Filter through a No. 41 Whatman filter paper and wash with hot water. Dissolve the hydroxide precipitate back into the original beaker with small portions of hot hydrochloric acid (1 to 2) and wash with hot hydrochloric acid (1 to 20). Dilute the filtrate to 200 ml., add 10 ml. of hydrochloric acid and boil several minutes. Determine the iron volumetrically in the usual manner by reducing with stannous chloride and titrating with 0.1 N dichromate in the usual manner.<sup>4</sup>

### Chromium

#### *Colorimetric (for 0.02-4% Chromium)*

Transfer a 50 ml. aliquot to a 600 ml. beaker. Add 20 ml. of sulphuric acid and dilute to 300 ml. with water. Heat to boiling and remove from the hot plate. Add a few drops of potassium permanganate solution (3%), 5

ml. of silver nitrate solution (1%), and 15 ml. ammonium persulphate solution (25%). Heat to boiling and boil at least 10 minutes. If the permanganate colour or the oxides of manganese do not persist, add 5 or 10 ml. more ammonium persulphate solution and boil another 10 minutes. Add 5 ml. of hydrochloric acid (1 to 3) and continue the boiling. If the permanganate colour does not disappear in 5 minutes, add an additional 3 ml. of hydrochloric acid (1 to 3). Boil for 10 minutes after the permanganate colour disappears. Cool to room temperature in a running water bath. Transfer to a 500 ml. volumetric flask and dilute to the mark. Allow to stand until the silver chloride precipitate has settled. Pipette an aliquot into a 50 ml. volumetric flask. Use a 10 ml. aliquot for 0.02-1% chromium, a 5 ml. aliquot for 1-2% chromium, and a 2 ml. aliquot for 2-4% chromium. If a 2 or 5 ml. aliquot is used, bring the volume to 10 ml. by the addition of dilute sulphuric acid (25 ml. per 500 ml.). Dilute to 40 ml. with water and add 2.0 ml. diphenylcarbazide solution (0.25%). Dilute to the mark and compare with a reagent blank at 580 m $\mu$  in 10-40 minutes.

For the preparation of the calibration curve, add 5 ml. dilute sulphuric acid (25 ml. per 500 ml.) to 50 ml. volumetric flasks. Add 0, 0.5, 1, 2, 3, 5, 8 and 10 ml. of standard chromate solution and proceed as above. Plot percentage transmittance against milligrams of chromium.

#### *Volumetric (for 0.1-10% Chromium)*

Pipette an aliquot into a 600 ml. beaker. Use a 100 ml. aliquot for 0.1-1% chromium, a 50 ml. aliquot for 1-5% chromium, and a 25 ml. aliquot for more than 5% chromium. Proceed as above to the point at which the solution has been cooled to room temperature following the oxidation with persulphate. Add a measured amount of ferrous ammonium sulphate solution and titrate with permanganate in the usual manner.<sup>2</sup>

### Tin

#### *Direct Volumetric (for more than 0.5% Tin)*

Transfer a 100 ml. aliquot to a 500 ml. Erlenmeyer flask. Add 100 ml. of water, 10 ml. of fluoboric acid (48%), 5 g. of iron powder, 2 drops of antimony trichloride solution (1%), and 60 ml. hydrochloric acid. Stopper with a tin head (a one-holed rubber stopper through which protrudes an L-shaped tube, the long arm of which dips to the bottom of a beaker filled with 10% sodium carbonate solution). Heat gently until the iron has dissolved and then boil about 2 minutes. Place flask in a cooling bath with the outlet of the tin head immersed in the sodium carbonate solution (10%). When the solution is cold, add a few marble chips and 5 ml. of starch solution (10%) and titrate rapidly with 0.02 N standard iodine solution to first faint blue. Deduct a blank, which is usually about 0.8 ml. Standardize the iodine by adding standard tin solution to 100 ml. portions of blank master solution and carrying the samples through the procedure.

#### *Volumetric-Hydrogen Sulphide Method (for 0.05-10% Tin)*

Transfer a 100 ml. aliquot to a 500 ml. Erlenmeyer flask. Add 3 ml. sulphuric acid and 10 ml. tartaric acid solution (20%). Add paper pulp and dilute to 300 ml. with water. Pass hydrogen sulphide through the solution for 15 minutes and allow to stand overnight. Filter through a No. 40 Whatman filter paper and wash with

sulphuric acid-hydrogen sulphide wash solution. Place filter paper and precipitate into the Erlenmeyer flask and add 15 ml. sulphuric acid, 25 ml. nitric acid and 3 ml. perchloric acid. Evaporate to fumes and continue heating strongly for 20 minutes to drive off the perchloric acid. Add 100 ml. water, 80 ml. hydrochloric acid, 2 ml. antimony trichloride solution (1%), and 8 g. of test lead. Dilute to 300 ml. with water, cover with a tin head, and boil 30 minutes. Cool and titrate as described above. Deduct a blank, which is usually 0.1 ml.

### Vanadium

Transfer a 100 ml. aliquot to a 400 ml. beaker. Add 3 ml. sulphuric acid and 2 ml. hydrofluoric acid. Heat to boiling, add 3 g. ammonium persulphate and boil for 5 minutes. Cool in a running water bath. Add 10–15 ml. 0.1 N ferrous ammonium sulphate solution and oxidize the vanadium by dropwise addition of potassium permanganate solution (5%). Maintain a pink colour for at least 10 minutes. Add sodium nitrite solution (5%) dropwise until the pink colour is destroyed. Add 3 g. urea and 4 ml. hydrofluoric acid. Allow to stand 5 minutes, and then add 1 ml. sodium diphenylbenzidine sulphionate solution (0.001 M). After 10 minutes, titrate with 0.02 N standard ferrous ammonium sulphate solution to a light green end point.

### Nitrogen

Pipette a 50 ml. aliquot into a semi-micro distillation apparatus. Add 25 ml. sodium hydroxide solution (40%). Distil into 10 ml. of boric acid solution (1%) and titrate with standard alkali in the usual manner.<sup>38</sup>

### Results

Colorimetric results for molybdenum in synthetic molybdenum-titanium alloys prepared by adding standard molybdenum solution to titanium are shown in Table VI. Colorimetric results for molybdenum in an actual molybdenum-titanium alloy are shown in Table VII. Colorimetric and gravimetric results for nickel in synthetic nickel-titanium alloys prepared by adding standard nickel solution to titanium are tabulated in Tables VIII and IX respectively. Colorimetric results for manganese in synthetic manganese-titanium alloys prepared by adding standard manganese solution to titanium are shown in Table X. Also in Table X are results that were obtained by adding weighed portions of high purity manganese metal to titanium. Colorimetric results for manganese in actual manganese-titanium alloys are shown in Table XI. No results are given for the other methods described in this paper, since the validity of these methods has been established by the various task forces sponsored by the Panel of Methods of Analysis of the Metallurgical Advisory Committee for Titanium. Mr. Sam Vigo, of Watertown Arsenal, is Chairman of this Panel.

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